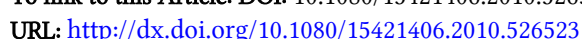


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# Tuning Helical Twisting Power of Isosorbide-Based Chiral Dopants by Chemical Modifications

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*Isosorbide-based chiral dopants (ICD) with various substituent groups were newly synthesized to control their helical twisting powers (HTP). Phase transition behaviors of ICD molecules were first investigated by combined techniques of differential scanning calorimetry, wide-angle X-ray diffraction, and cross-polarized optical microscopy. ICD with n-hexyloxy end groups formed the multiple ordered phases, and those with methoxy or acetoxy end groups exhibited a simple crystal-to-isotropic transition. Energy-minimized chemical conformations of ICD molecules revealed that all the ICDs had twisted conformations and that the extension of the benzoyl ester moiety induced a higher twisted conformation. By varying substitution groups, HTPs of ICDs were controlled from 26.6 to 80.2  $\mu\text{m}^{-1}$ . Particularly, ICD with an acetoxy end group (ICD-2) showed the largest HTP. It was also realized that by controlling the content of ICD-2 from 3.0 to 4.5 mol%, the helical pitch length of cholesteric LC mixture was adjusted to reflect a specific visible light.*

**Keywords** Chiral dopants; cholesteric liquid crystal; helical twisting power; isosorbide

## Introduction

Cholesteric liquid crystals (CLCs) are optically active variants of nematic (N) LC compounds, which are also called the chiral nematic (N\*) LCs. The cholesteric phase is readily developed by the addition of a chiral compound as a dopant into the achiral N LC host. By incorporating a chiral moiety to LC molecules, LC twists perpendicular to its director and forms the N\* phase. If the helical pitch, the distance over which the LC molecules undergo a full 360° twist, is the same order of magnitude as the wavelength of visible light, CLCs can reflect a corresponding color [1,2].

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Therefore, they can be used in LCDs and other related applications such as reflectable polarizers, color filters, and chiral polymer films to improve viewing angles [3–7].

Because the cholesteric phase can be induced simply by adding a chiral dopant into an N LC host, the helical pitch length of the CLC can be adjusted by the concentration of chiral dopant and by the helical twisting power (HTP) change of the chiral dopant itself [8]. However, an excess amount of chiral dopant can decrease the isotropic (I)-to-N phase transition temperature and a highly viscous LC mixture and undesirable precipitation may occur because the solubility of chiral dopant in the LC host is limited [9–11]. Therefore, it is essential that a high degree of twist should be obtained from a limited amount of chiral dopant to avoid perturbing the original properties of LC host materials. There have been many efforts to develop a chiral dopant with a high HTP and a good solubility and without any changes of the properties of host materials [12,13]. According to the chemical structures, the chiral dopants can be classified to three different types [14]. The first type of chiral dopant contains chiral centers at its alkyl chain, which makes it possible to introduce two or more chiral centers to a single molecule. Secondly, a chiral center can be located in the flexible spacer chain between two mesogen core units to form the structure like a dimer or a twinned molecule. Finally, a chiral center can be incorporated in the mesogen core unit. This final type of chiral dopant shows the greatest coupling effect between the chiral center and core, which results in a high HTP [14–16]. Isosorbide (1,4:3,6-dianhydro-D-sorbitol) is the most well-known chiral compound for the third type of chiral dopants. Generally, isosorbide-based chiral dopants (ICD) are able to generate large HTPs, however, their poor solubility in LC hosts is a drawback for their application as chiral dopants [17–19]. In this article, we newly designed and synthesized a series of ICDs with various substituent groups into the 2-OH and 5-OH positions of isosorbide. Amplification of HTPs and phase transition behaviors of ICDs were also investigated.

## Experiments

### Materials

1,4:3,6-Dianhydro-D-sorbitol (D-isosorbide, 98%, Aldrich) was used as a core material. Hydroxybenzoic acid (99%, Aldrich, Milwaukee, WI, USA), acetic anhydride (99%, Aldrich, Milwaukee, WI, USA), thionyl chloride (99%, Aldrich, Milwaukee, WI, USA), 4-methoxy benzoylchloride (99%, Aldrich), and 4-(hexyloxy) benzoic acid (98%, Aldrich, Milwaukee, WI, USA) were used for introducing different substituent groups. Tetrahydrofuran (THF), pyridine, toluene, and dichloromethane (DCM) were used as solvents. All reagents and solvents were reagent grade and were used without further purification. LC242 (BASF, Ludwigshafen, Germany) was used as a host LC for preparing a CLC film.

### Synthetic Procedure of Chiral Dopants (ICD)

*1,4:3,6-Dianhydro-D-sorbitol-2,5-bis(4-(4-methoxybenzyloxy) Benzoate) (ICD-1).* 4-Hydroxybenzoic acid (2.72 g; 19.7 mmol) and acetic anhydride (5.10 g; 50 mmol) were dissolved in THF with pyridine. The reaction mixture was stirred at room temperature for 24 h. After reaction, pure water and 1 N HCl were added to form a precipitate. The resulting suspension was filtered and the resulting solid was

recrystallized with deionized water and ethanol to produce acetoxybenzoic acid (**1**) in 80% yield. Prepared **1** (10 g; 55.51 mmol) and thionyl chloride (60 mL; 0.83 mol) with small drops of toluene were refluxed. After 3 h, thionyl chloride was distilled under reduced pressure and the remaining thionyl chloride was completely removed by azeotropic distillation with toluene to afford the desired compound **2** in 75% yield. Then, **2** (11.02 g; 55.49 mmol) was coupled with D-isosorbide (3.86 g; 26.41 mmol) in THF with pyridine. After stirring at room temperature for 10 h, the resulting solid was reprecipitated with deionized water and methanol in 85% yield. Finally this compound (10 g; 21.26 mmol) was dissolved in ethanol and stirred for 2 h with sodium hydroxide solution (1.7 g; 42.5 mmol). After a dilute HCl solution was added, compound **3** was obtained in 87% yield by recrystallization of the crude product with deionized water and methanol. Compound **3** (5 g; 12.9 mmol) and 4-methoxy benzoylchloride (4.84 g; 28.28 mmol) were dissolved in THF with pyridine (2.46 g; 31 mmol) and stirred at room temperature for 12 h. The resulting solid was reprecipitated with deionized water and methanol to give ICD-1 in 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18–8.15 (m, 6H), 8.11 (d,  $J = 8.5$  Hz, 2H), 7.32 (dd,  $J_1 = 11.4$  Hz,  $J_2 = 8.7$  Hz, 4H), 7.01 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.3$  Hz, 4H), 5.52 (s, 1H), 5.45 (q,  $J = 5.3$  Hz, 1H), 5.09 (t,  $J = 5.0$  Hz, 1H), 4.71 (d,  $J = 4.7$  Hz, 1H), 4.14 (s, 2H), 4.12–4.06 (m, 2H), 2.36 (s, 6H); Anal. Calc. for  $\text{C}_{36}\text{H}_{30}\text{O}_{12}$ : 654.2; Found: ESI-MS,  $m/z$ , positive  $[\text{M} + \text{H}]^+$ : 665.

*1,4:3,6-Dianhydro-D-sorbitol-2,5-bis(4-(4-acetoxybenzoyloxy) benzoate) (ICD-2).* Compound **3** (5 g; 12.9 mmol) and 4-(chlorocarbonyl)phenyl acetate (5.46 g; 27.49 mmol) were dissolved in THF with pyridine. The reaction mixture was stirred at room temperature for 12 h. The resulting crude product was purified by recrystallization with deionized water and ethanol to give ICD-2 in 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.25 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 5.4$  Hz, 4H), 8.19 (d,  $J = 8.6$  Hz, 2H), 8.12 (d,  $J = 8.6$  Hz, 2H), 7.33 (dd,  $J_1 = 11.6$  Hz,  $J_2 = 8.7$  Hz, 4H), 7.28 (d,  $J = 2.2$  Hz, 2H), 5.52 (s, 1H), 5.46 (q,  $J = 5.3$  Hz, 1H), 5.09 (t,  $J = 5.0$  Hz, 1H), 4.71 (d,  $J = 4.6$  Hz, 1H), 4.14 (s, 2H), 4.12–4.06 (m, 2H), 3.91 (s, 6H); Anal. Calc. for  $\text{C}_{38}\text{H}_{30}\text{O}_{14}$ : 710.2; Found: ESI-MS,  $m/z$ , positive  $[\text{M} + \text{H}]^+$ : 711.

*1,4:3,6-Dianhydro-D-sorbitol-2,5-bis(4-(4-(Hexyloxy)benzoyloxy) benzoate) (ICD-3).* 4-(Hexyloxy)benzoyl chloride was prepared in advance of ICD-3 synthesis. 4-(Hexyloxy) benzoic acid (5 g; 22.5 mmol) and thionyl chloride (50 mL; 0.69 mol) with small drops of toluene were refluxed. After 3 h, thionyl chloride was distilled under reduced pressure and the remaining thionyl chloride was completely removed by azeotropic distillation with toluene. Compound **3** (5 g; 12.9 mmol) and pyridine (2.46 g; 31 mmol) were dissolved in THF and then 4-(hexyloxy)benzoyl chloride (6.83 g; 28.38 mmol) was added drop wise. The reaction mixture was stirred at room temperature for 12 h. The resulting crude product was purified by recrystallization with deionized water and ethanol to give ICD-3 in 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18–8.14 (m, 6H), 8.11 (d,  $J = 8.7$  Hz, 2H), 7.32 (dd,  $J_1 = 11.5$  Hz,  $J_2 = 8.8$  Hz, 4H), 6.99 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.5$  Hz, 4H), 5.52 (s, 1H), 5.45 (q,  $J = 5.2$  Hz, 1H), 5.09 (t,  $J = 5.0$  Hz, 1H), 4.71 (d,  $J = 4.7$  Hz, 1H), 4.14–4.05 (m, 8H), 1.84 (p,  $J = 6.8$  Hz, 4H), 1.49 (p,  $J = 7.0$  Hz, 4H), 1.37–1.36 (m, 8H), 0.94–0.92 (m, 6H); Anal. Calc. for  $\text{C}_{46}\text{H}_{50}\text{O}_{12}$ : 794.3; Found: ESI-MS,  $m/z$ , positive  $[\text{M} + \text{H}]^+$ : 794.

*1,4:3,6-Dianhydro-D-sorbitol-2,5-bis(4-acetoxybenzoate)* (ICD-4). D-Isosorbide (5 g; 34.2 mmol) and pyridine (5.95 g; 75.24 mmol) were dissolved in THF. 4-Chlorocarbonylphenyl acetate (14.3 g; 71.82 mmol) was added drop wise to the reaction mixture and stirred at room temperature for 12 h. The resulting crude product was purified by recrystallization with methanol to give ICD-4 in 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12 (d,  $J = 8.6$  Hz, 2H), 8.06 (d,  $J = 8.6$  Hz, 2H), 7.19 (dd,  $J_1 = 11.8$  Hz,  $J_2 = 8.6$  Hz, 4H), 5.49 (s, 1H), 5.43 (q,  $J = 5.3$  Hz, 1H), 5.06 (t,  $J = 5.0$  Hz, 1H), 4.67 (d,  $J = 4.7$  Hz, 1H), 4.10–4.03 (m, 4H), 2.33 (d,  $J = 16.6$  Hz, 6H); Anal. Calc. for  $\text{C}_{24}\text{H}_{22}\text{O}_{10}$ : 470.1; Found: ESI-MS,  $m/z$ , positive  $[\text{M} + \text{H}]^+$ : 471.

*1,4:3,6-Dianhydro-D-sorbitol-2,5-bis(4-hexyloxybenzoate)* (ICD-5). D-Isosorbide (5 g; 34.2 mmol) and pyridine (5.95 g; 75.24 mmol) were dissolved in THF. 4-Hexyloxybenzoyl chloride (17.3 g; 71.82 mmol) was added drop wise to the reaction mixture and stirred at room temperature for 12 h. The resulting crude product was purified by recrystallization with methanol to give ICD-5 in 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (d,  $J = 8.8$  Hz, 2H), 7.96 (d,  $J = 8.8$  Hz, 2H), 6.91 (dd,  $J_1 = 13.4$  Hz,  $J_2 = 8.8$  Hz, 4H), 5.46 (d,  $J = 3.0$  Hz, 1H), 5.40 (q,  $J = 5.3$  Hz, 1H), 5.04 (t,  $J = 5.0$  Hz, 1H), 4.68 (d,  $J = 4.6$  Hz, 1H), 4.14–4.07 (m, 3H), 4.03–4.00 (m, 5H), 1.83–1.78 (m, 4H), 1.47–1.46 (m, 4H), 1.36–1.35 (m, 8H), 0.93–0.91 (m, 6H); Anal. Calc. for  $\text{C}_{32}\text{H}_{42}\text{O}_8$ : 554.3; Found: ESI-MS,  $m/z$ , positive  $[\text{M} + \text{H}]^+$ : 555.

### Fabrication of CLC Cells

Glass substrates were cleaned with a display-grade detergent solution. They were rinsed with acetone and isopropyl alcohol using an ultrasonic cleaner for 15 and 20 min, respectively. LC alignment layer (Nissan SE6414, Tokyo, Japan) was introduced on the glass substrate by spin-coating and was thermally cured at 225°C. Its surface was rubbed with a velvet cloth. The CLC solution including LC242, chiral dopant, photoinitiator (Irgacure 907, Ciba, Basel, Switzerland), and solvent was spin-coated on the alignment layer at 450 rpm for 20 s and then at 2,800 rpm for 40 s. A stable CLC film was obtained by ultraviolet (UV) curing after solvent evaporation. UV curing was performed at an irradiation intensity of 20 mW/cm<sup>2</sup> for 60.

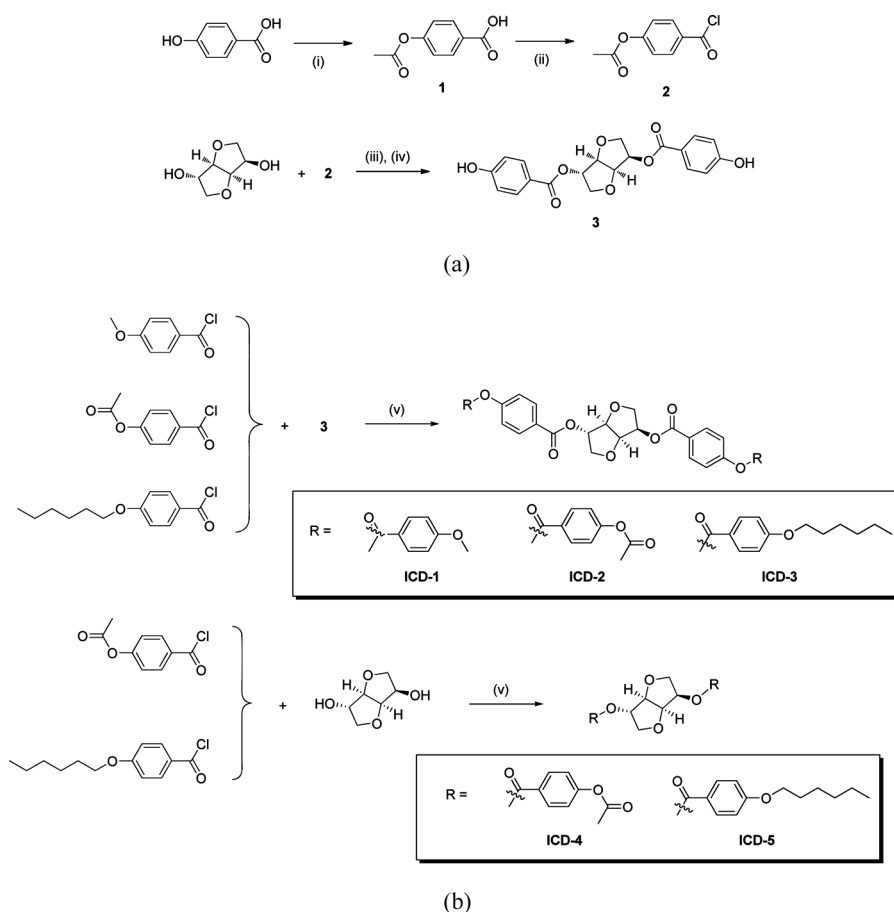
### Measurements

All newly synthesized compounds were identified by nuclear magnetic resonance (NMR) and mass spectrometers. The  $^1\text{H}$ -NMR spectra were measured using a Bruker-600 (MHz) spectrometer with a tetramethylsilane (TMS), peak as a reference. Mass spectra were recorded on a JEOL JMS-600 W spectrometer. The thermal transition of products was investigated with a Shimadzu D-60 differential scanning calorimeter (DSC) at a heating and cooling rate of 5 K min<sup>-1</sup>. The phase transitions were examined by a Nikon 100POL polarized optical microscope (POM) equipped with Mettler Toledo hot-stage FP-82 heating and cooling stage with temperature controller. Wide-angle X-ray diffraction analyses were performed with a Bruker GADDS instrument with 2 theta range of 0–40 and exposure time of 1,200 s.

## Results and Discussion

### Preparation of Chiral Dopants

Five isosorbide-based chiral dopants (ICD-1, ICD-2, ICD-3, ICD-4, ICD-5) were designed and synthesized. Isosorbide itself and isosorbide derivative (**3**) extended with a 4-hydroxybenzoyl group at the 2-OH and 5-OH positions of isosorbide were used as chiral mesogen core units. In order to prepare the isosorbide derivative (**3**), 1,4:3,6-dianhydro-D-sorbitol-2,5-bis(4-acetoxybenzoate) (**2**) was synthesized from 4-hydroxybenzoic acid via a two-step reaction including a protection reaction of 4-hydroxy group with acetyl group and an acid chloride formation reaction, followed by coupling with isosorbide to afford compound **3** (Scheme 1a). The synthetic isosorbide derivative (**3**) was attached three different substituent groups corresponding to 4-methoxybenzoyl, 4-acetylbenzoyl, and 4-hexyloxybenzoyl groups to obtain ICD-1,

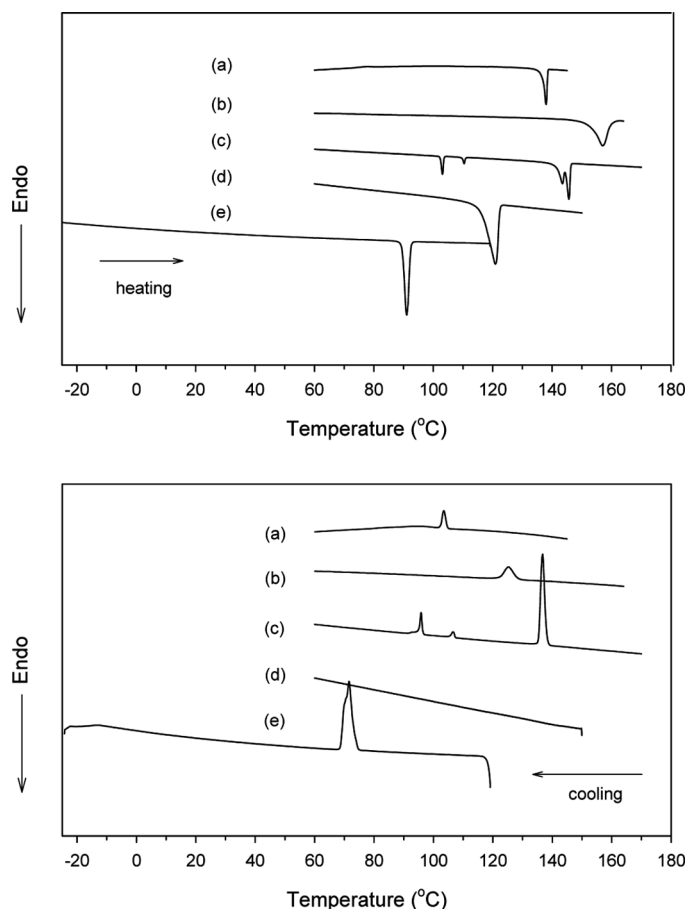


**Scheme 1.** Synthetic routes for (a) 1,4:3,6-dianhydro-D-sorbitol-2,5-bis(4-hydroxybenzoate) (**3**) and (b) chiral dopants carrying different substituent groups: (i) acetic anhydride, pyridine, THF, room temperature, 24 h, 80%; (ii)  $\text{SOCl}_2$ , toluene, reflux, 3 h, 75%; (iii) pyridine, THF, room temperature, 10 h, 85%; (iv) NaOH, ethanol, room temperature, 2 h, 87%; (v) pyridine, THF, room temperature, 12 h.

ICD-2, and ICD-3, respectively. ICD-4 and ICD-5 were synthesized by the direct attachment of 4-acetylbenzoyl and 4-hexyloxybenzoyl groups onto isosorbide (Scheme 1b).

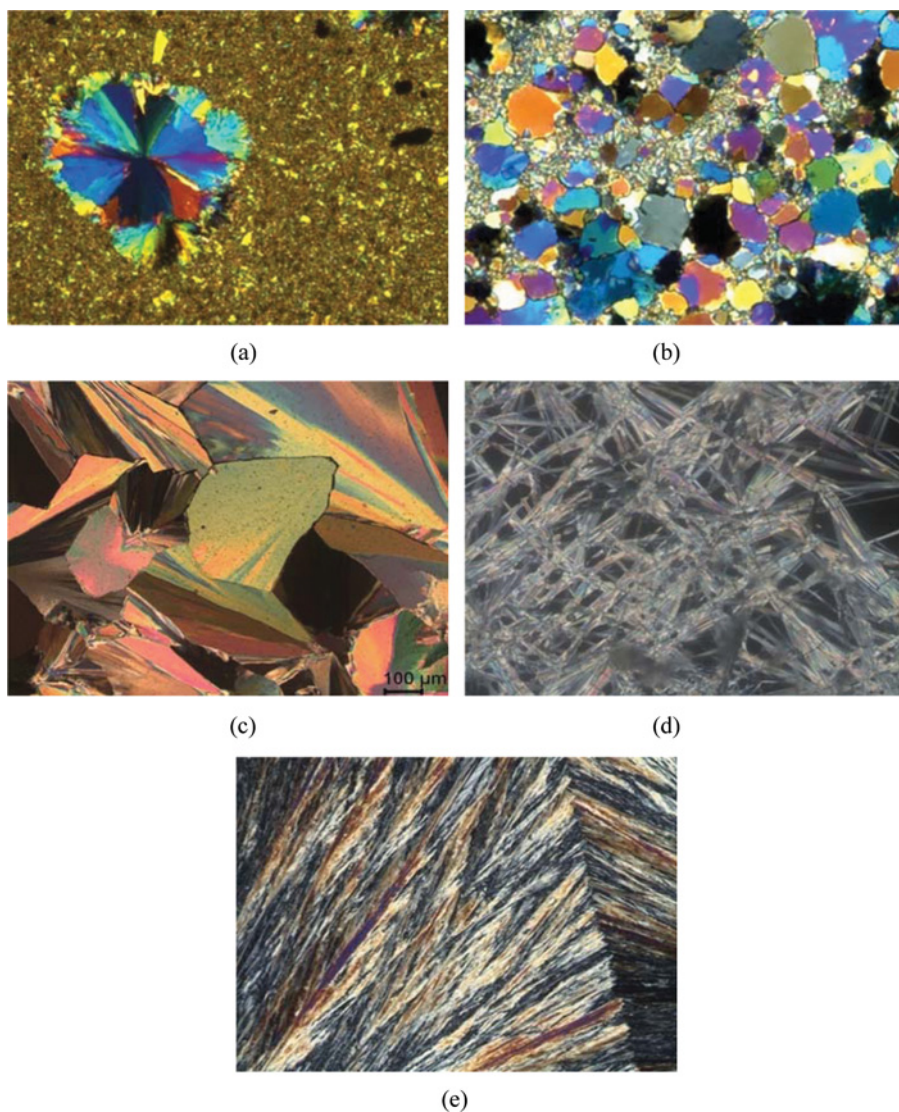
### Phase Transition of Chiral Dopants

Phase transition behaviors of synthetic chiral dopants were characterized with DSC and POM equipped with a heat processor. DSC thermograms were obtained during the second heating and cooling cycles (Fig. 1). They showed that only ICD-3 showed multiple transition peaks in DSC thermograms. Their phase transition temperatures were as follows: Cr  $\rightarrow$  103°C  $\rightarrow$  LC1\*  $\rightarrow$  110°C  $\rightarrow$  LC2\*  $\rightarrow$  146°C  $\rightarrow$  I and I  $\rightarrow$  137°C  $\rightarrow$  LC2\*  $\rightarrow$  107°C  $\rightarrow$  LC1\*  $\rightarrow$  96°C  $\rightarrow$  Cr in the heating and cooling processes, respectively (Fig. 1c). In this notation, Cr, LC\*, and I stand for crystal, liquid crystal, and isotropic phases, respectively. POM photographs of ICD-3 at 110°C during the cooling process showed that ICD-3 seemed to have a mosaic texture of



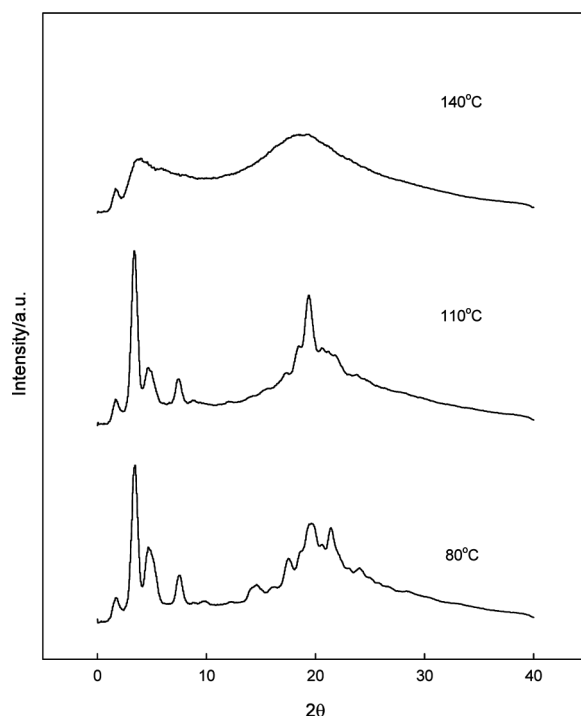
**Figure 1.** Differential scanning calorimetric (DSC) heating (upper) and cooling (bottom) scans of (a) ICD-1, (b) ICD-2, (c) ICD-3, (d) ICD-4, and (e) ICD-5 at 5°C/min heating rate. A DSC thermogram of ICD-4 was obtained in the first cooling and second heating process.

soft crystal (Fig. 2c). In order to confirm the existence of LC phases of ICD-3, XRD analysis was performed. XRD spectra of ICD-3 showed that very strong diffraction peaks at  $3.4^\circ$ ,  $4.7^\circ$  and  $7.5^\circ$  were observed during the cooling process. Especially, the peaks at  $3.4^\circ$  and  $19.4^\circ$  increased at  $110^\circ\text{C}$  and then decreased with cooling (Fig. 3). Based on the experimental results of DSC and POM combined with those of XRD, it was realized that the LC phase in ICD-3 is not a simple low-ordered LC phase, such as N or smectic A but a highly ordered LC phases. This means that there are no long-range positional orders in three dimensions like a true crystal. This argument



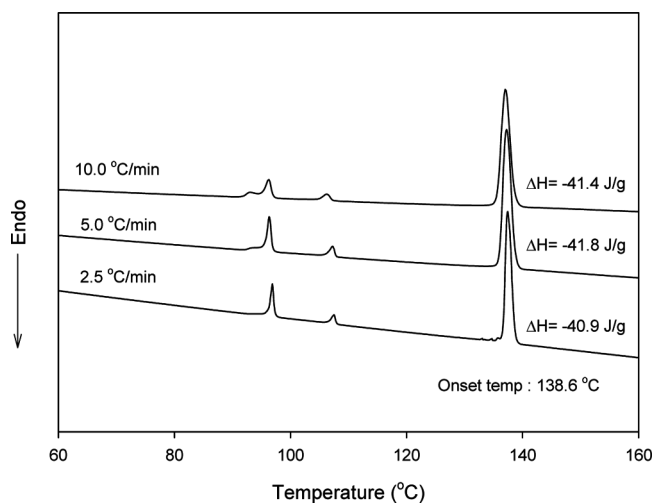
**Figure 2.** POM microphotographs of (a) ICD-1 taken at  $80^\circ\text{C}$  in the cooling process, (b) ICD-2 taken at  $90^\circ\text{C}$  in the cooling process, (c) ICD-3 taken at  $110^\circ\text{C}$  in the cooling process, (d) ICD-4 taken at  $55^\circ\text{C}$  in the heating process, (e) ICD-5 taken at  $65^\circ\text{C}$  in the cooling process. Magnification of all POM microphotographs is  $100\times$ .





**Figure 3.** XRD patterns of ICD-3 measured at 140°C, 110°C, and 80°C in the cooling process.

was also supported by DSC experiments with different cooling and subsequent heating rates. The transition temperature and associated enthalpy change, measured by DSC, between I and LC2\* and those between LC2\* and LC1\* were not highly dependent on the cooling rate (Fig. 4). This supports that ICD-3 had highly ordered LC phases. In contrast, ICD-1, ICD-2, ICD-4, and ICD-5 showed a simple Cr-to-I transition. ICD-1 showed phase transitions as follows: Cr  $\rightarrow$  138°C  $\rightarrow$  I in the heating process and I  $\rightarrow$  104°C  $\rightarrow$  Cr in cooling process (Fig. 1a). POM texture of ICD-1 taken at 80°C in the first cooling process suggested that ICD-1 had a commonly observed crystalline phase (Fig. 2a) [20]. ICD-2 had Cr  $\rightarrow$  157°C  $\rightarrow$  I and I  $\rightarrow$  125°C  $\rightarrow$  Cr transitions in the heating and cooling processes, respectively (Fig. 1b). The POM photographic image of ICD-2 taken at 90°C in the cooling process showed a mosaic phase pattern, which was commonly observed as a soft crystal phase (Fig. 2b). The phase transition temperatures of ICD-5 were as follows: Cr  $\rightarrow$  89°C  $\rightarrow$  I and I  $\rightarrow$  74°C  $\rightarrow$  Cr in the heating and cooling process, respectively (Fig. 1e). The POM photograph of ICD-5 showed needle-like structures growing from the I melt when it was cooled to lower than 70°C (Fig. 2e). In case of ICD-4, it showed a Cr  $\rightarrow$  121°C  $\rightarrow$  I and no thermal transition in the cooling process (Fig. 1d). Crystallization transition of ICD-4 was not observed in our experimental condition. However, it showed a melting transition in the following heating process with a stay at room temperature. This indicates that ICD-4 was very slowly crystallized; therefore, an annealing process was required to obtain the crystalline phase. The formation of crystal of ICD-4 was confirmed by the POM morphology at 55°C, exhibiting needle-like crystals (Fig. 2d).

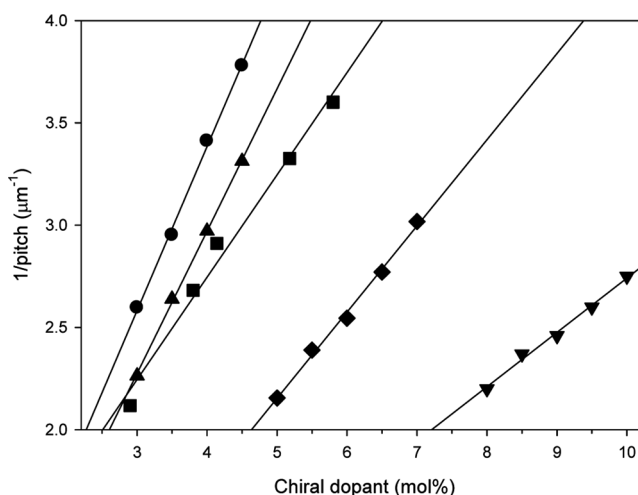


**Figure 4.** DSC thermograms of ICD-3 obtained in the first cooling process with different cooling rates: 2.5°C /min, 5.0°C/min, and 10.0°C/min.

### Determining HTP of Chiral Dopants

HTPs of chiral dopants were determined by a selective light reflection method that is suitable for measuring HTP of a chiral dopant when the helical pitch of CLC film is smaller than 1  $\mu\text{m}$  [21, 22]. From the selective light reflection method, the helical pitch of CLC film ( $p$ ) is obtained by following equation

$$\lambda_{\text{max}} = n \times p \quad (1)$$



**Figure 5.** Helical pitch length of CLC films fabricated with chiral dopants as a function of their concentration (ICD-1: square, ICD-2: circle, ICD-3: triangle up, ICD-4: triangle down, ICD-5: diamond).

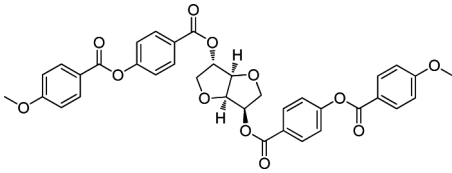
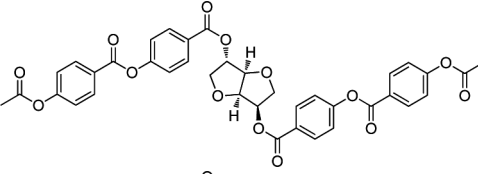
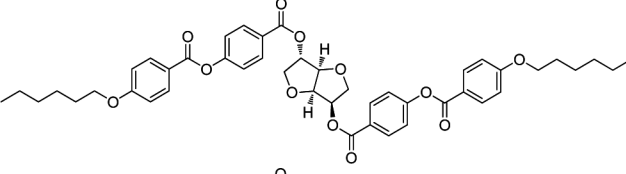
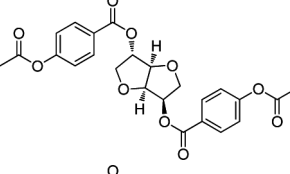
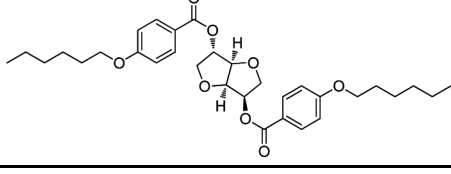
where  $\lambda_{\text{max}}$  is the maximum wavelength for the reflected light and  $n$  is the mean refractive index of CLC film. The average refractive indices of CLC films fabricated with each chiral dopant were measured with a prism coupler. The  $\lambda_{\text{max}}$  of a reflected light was measured by a UV-Vis spectrometer.

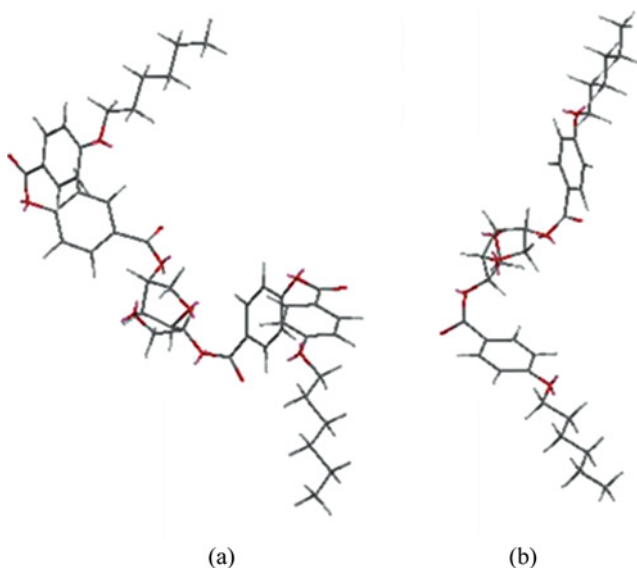
According to De Gennes and Prost [23], the pitch of CLC ( $p$ ) is related to the macroscopic HTP and the concentration of a chiral dopant ( $X_c$ ) by

$$1/p = \text{HTP} \times X_c \tag{2}$$

The inverse of pitch ( $1/p$ ) was first plotted as a function of the mole fraction of five synthetic chiral dopants (ICD-1, ICD-2, ICD-3, ICD-4, ICD-5). According to Eq. (2), HTPs of synthetic chiral dopants were obtained from a slope of the linear relationship between  $1/p$  and  $X_c$  in the low concentration regime (Fig. 5). The measured HTPs are listed in Table 1. HTPs are variable from 26.6 to 80.2  $\mu\text{m}^{-1}$  depending on the substituent groups. ICD-1, ICD-2, and ICD-3 synthesized from extended isosorbide showed relatively higher HTPs than ICD-4 and ICD-5 synthesized directly from isosorbide. Comparing the HTPs of chiral dopants having the same tail

**Table 1.** Helical twisting powers (HTP) of synthetic chiral dopants

ID	Chemical structure	HTP ( $\mu\text{m}^{-1}$ )
ICD-1		50.0
ICD-2		80.2
ICD-3		69.6
ICD-4		26.6
ICD-5		42.1



**Figure 6.** Molecular structures of (a) ICD-3 and (b) ICD-5 obtained by energy minimization iteration.

parts (ICD-2 vs. ICD-4 or ICD-3 vs. ICD-5), it is clear that the extension of the aromatic part increased the HTP. This seems to be due to the highly twisted conformation by the additional benzoyl ester moieties, which could be preliminarily confirmed with molecular structures of ICD-3 and ICD-5 obtained by energy minimization iteration (Fig. 6). This result suggests that more twisted chiral dopants are preferable to get a higher HTP. Likewise, the tail parts of chiral dopants are also able to affect the HTPs when they could twist themselves or cooperatively twist with their neighbor molecules. ICD-1, ICD-2, and ICD-3 have the same core unit structure but their HTP values were  $50.0\ \mu\text{m}^{-1}$  for ICD-1,  $80.2\ \mu\text{m}^{-1}$  for ICD-2, and  $69.9\ \mu\text{m}^{-1}$  for ICD-3. From these results, it was found that the acetoxy group is more effective than the alkoxy group for transferring a twisting torque of a chiral compound to an LC host molecule.

Interestingly, CLC film fabricated with ICD-2 was *ca.* 30% thicker than CLC films fabricated with ICD-1 and ICD-3. When identical amounts (4 mol%) of ICD-1, ICD-2, and ICD-3 were added under the same processing conditions, the average film thicknesses measured by the prism coupler were  $1.81\ \mu\text{m}$  for ICD-1,  $2.41\ \mu\text{m}$  for ICD-2, and  $1.87\ \mu\text{m}$  for ICD-3. This result implies that ICD-2 induced a stronger interaction with the host LC molecule than the other two chiral dopants. In addition, hexyloxy-substituted ICD-3 showed a little bit larger HTP than that of methoxy-substituted ICD-1. We believe that the relatively longer alkyl chain caused a more twisted structure in the equilibrium state.

### CLC Film Properties

The CLC films that can possess pitches comparable to the wavelength of visible light were prepared by adding a low percentage of ICD-2. CLC films selectively reflecting the blue color ( $\lambda_{\text{max}} = 462\ \text{nm}$ ) were fabricated by mixing 4.0 mol% of ICD-2 with a

LC242. In contrast, 5.2 mol% of ICD-1 and 4.5 mol% of ICD-3 were required to make CLC films whose  $\lambda_{\max}$  were 470 nm. All of the chiral dopants did not cause a solubility problem in making CLC films within this amount.

ICD-4, however, induced a CLC film reflecting the green color ( $\lambda_{\max} = 568$  nm) by adding 10 mol% to LC242. More than 10 mol% of ICD-4 was necessary to fabricate a CLC film that reflects a blue light. When the amount of ICD-4 exceeded 10 mol%, ICD-4 began to be crystallized. This crystallization may be due to poor solubility with LC242.

## Conclusion

A series of isosorbide-based chiral dopants (ICD-*n*, *n* = 1–5) was newly designed and synthesized, and then CLC phases were obtained by mixing them with a host N LC (LC242). Depending on their substituent groups, ICD-*n* showed various phase transition behaviors. ICD with a hexyloxy end group induced multiple phase transitions, whereas ICD with a methoxy and acetoxy end groups exhibited a simple Cr-to-I transition. From the evaluated HTP results combined with energy-minimized chemical conformations, it was realized that HTPs of ICDs were closely related to the substituent groups. When the substituent caused a higher twisted structure and a good interaction with a host nematic LC molecule, HTP of ICDs became larger. In a series of ICDs, ICD-2 with acetoxy as an end group showed the highest HTP value of  $80.2 \mu\text{m}^{-1}$ , although it had a less twisted structure than ICD-3. This means that acetoxy is more effective than alkyloxy groups for transferring a twisting torque of a chiral dopant to an LC host molecule. Furthermore, the helical pitches of the CLCs were tuned to reflect a specific visible light by varying the content of ICD-2 from 3.0 to 4.5 mol%.

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