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Title: Chirality transfer from atropisomeric chiral inducers to nematic and smectic liquid crystals – synthesis and characterization of *di*- and *tetra*-substituted axially chiral binaphthyl derivatives

Fingerprint (lower) and striated fan-shape (upper) textures of chiral nematic (N\*) and chiral smectic C (S<sub>C</sub>\*) liquid crystals (LCs) are induced by addition of atropisomeric chiral dopant [binaphthyl derivative] (center of circle) to host nematic LC [5CB] with Schlieren texture (lower, background) and smectic C LC [PhB1 or PhB2] with fan-shaped texture (upper background).

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PAPER

# Chirality transfer from atropisomeric chiral inducers to nematic and smectic liquid crystals – synthesis and characterization of *di*- and *tetra*-substituted axially chiral binaphthyl derivatives<sup>†</sup>

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The chirality transfer of axially chiral binaphthyl derivatives bearing liquid crystal (LC) moieties at the n,n' positions (n = 3, 4, 6) of the binaphthyl rings to nematic (N) and smectic (S) LCs is investigated. Chiral nematic LCs (N\*-LCs) are prepared by adding a small amount of the chiral binaphthyl derivative into host N-LCs composed of cyanobiphenyl mesogen cores. The binaphthyl derivative with phenylcyclohexyl (PCH) type LC moieties at the 4,4' positions of the binaphthyl ring [**D-4,4'**] exhibits a low helical twisting power (HTP) of 11  $\mu$ m<sup>-1</sup>. In contrast, those with LC moieties at the 3,3' and 6,6' positions of the binaphthyl rings [**D-3,3'** and **D-6,6'**] exhibit high HTPs of 153  $\mu$ m<sup>-1</sup> and 154  $\mu$ m<sup>-1</sup>, respectively. Next, the binaphthyl derivatives are added into two types of S-LCs with phenylbenzoate mesogen cores: 4-(4-methylpentyloxy)phenyl-4-(decyloxy)benzoate [**PhB1**] and 4-(3-methylpentyloxy) phenyl-4-(decyloxy)benzoate [**PhB2**]. The mixture of the host LC, **PhB1** or **PhB2** with the chiral dopant, **D-3,3'** or **D-6,6'** shows chiral smectic LCs C (S<sub>C</sub>\*-LCs). The highly twisted S<sub>C</sub>\* phases with helical pitches of 1.2–1.4  $\mu$ m are prepared in **PhB1** and **PhB2** by using the chiral dopant of **D-6,6'**. It is concluded that **D-6,6'** has a large helical twisting power and is the most favourable atropisomeric chiral inducer for chirality transfer to both N-LCs and S-LCs.

#### 1. Introduction

Chirality is a very intriguing issue in liquid crystal (LC) science.<sup>1</sup> There are many types of chiral LCs, such as chiral nematic (N\*),<sup>2</sup> chiral smectic C  $(S_C^*)$ ,<sup>3</sup> blue phase,<sup>4</sup> and twisted grain boundary (TGB) phase LCs.<sup>5</sup> Chiral inductions in nematic (N) and smectic  $C(S_C)$  LCs through chirality transcription by the chiral dopants have been extensively investigated.<sup>6-11</sup> The chiral nematic liquid crystal (N\*-LC) is prepared by adding a small amount of a chiral compound as a chiral dopant (a chiral inducer) to N-LC. Additionally, the helical pitch of the N\*-LC can be controlled by changing the concentration of the chiral dopant, modifying the helical twisting power (HTP) of the chiral dopant,12 and even using chirality-switchable chiral dopants that are responsive to external stimuli, such as thermal heating<sup>13</sup> and light irradiation.<sup>14</sup> N\*-LCs have recently been identified as useful as asymmetric reaction fields for the synthesis of one-handed helical conjugated polymers.<sup>12a,15</sup> Because the helical sense and pitch of the polymers strongly depend on those of the N\*-LCs, understanding the potential abilities of the chiral dopants is essential. There are two main types of chiral dopants: asymmetric centre and axially chiral compounds. The latter is more promising than the former because of its large HTP and ready chemical modification, allowing the HTP to be tuned. In fact, chiral binaphthyl derivatives bearing *di*- or *tetra*-substituents at various positions of the binaphthyl rings are preferably used as chiral dopants. However, how the substituents at the binaphthyl rings affect the chirality transfer of the chiral compound to the host LCs remains unclear.

Some S<sub>C</sub>\*-LCs have been used as ferroelectric materials that quickly respond to an electric field owing to their substantially large spontaneous polarisation. Although it is possible to induce a S<sub>C</sub>\* phase by adding a chiral dopant into a S<sub>C</sub>-LC, the formation of the S<sub>C</sub>\* phase is not always guaranteed.<sup>16</sup> The difficulty of chirality transfer and/or chirality induction of the chiral dopant to the host  $S_{C}$ -LC is due in part to (i) the chiral dopant's low miscibility in the S<sub>C</sub>-LCs and (ii) rigidity from the highly ordered structure of the S<sub>C</sub>-LC. The former issue (low miscibility) can be overcome by introducing LC groups as substituents into the chiral dopant, which should enhance the miscibility between the chiral dopant and the S<sub>C</sub>-LC. The latter (rigidity) can be resolved by choosing chiral compounds with large HTPs, such as axially chiral binaphthyl derivatives. However, one issue remains to be settled. In the  $S_C^*$  phase, the director (n) is tilted with respect to the layer normal and precesses simultaneously about the layer normal. At the present time, it is still unclear how the tilt angle ( $\theta$ ), defined between the director (n)

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and the layer normal, and the precessing motion about the layer normal together produce the helical structure of the  $S_C^*$  phase, although the spontaneous polarisation has been elucidated to be proportional to the sine of the tilt angle.

The axially chiral binaphthyl derivatives are typical atropisomers that are conformers arising from restricted rotation about a single bond and can be regarded as chirality sources for asymmetric catalysts, chiral recognition, and chiral oligomers and polymers.<sup>17</sup> The HTPs of the binaphthyl derivatives come from dual steric repulsions between substituents at the 2,2' positions and those between hydrogen atoms at the 8,8' positions of the naphthyl rings.<sup>2</sup> Moreover, the substituents can be inserted at various positions of the binaphthyl rings. In fact, many binaphthyl derivatives with different substituents at the 2,2',<sup>12,13c,18</sup> 2,2',6,6';<sup>12,19</sup> or 2,2',5,5',6,6' positions<sup>20</sup> have been synthesised. However, few studies comprehensively address the relationship between the substitution positions of the binaphthyl ring and the effectiveness of the chirality transcription to N- and S<sub>C</sub>-LCs.

In this study, we have synthesised a series of axially chiral binaphthyl derivatives bearing phenylcyclohexyl (PCH) type LC groups at the *n*,*n'* positions (*n* = 3, 4 and 6) of the binaphthyl rings and investigated their chirality transcription abilities as chiral dopants to induce N\*- and S<sub>C</sub>\*-LCs. The binaphthyl derivative of **D-6,6'**, having a direct linkage between the mesogenic core of the LC substituents and the binaphthyl rings at the 6 and 6' positions, exhibits a large HTP of 154  $\mu$ m<sup>-1</sup> in N-LC and is capable of inducing the S<sub>C</sub>\* phase with a helical pitch of 1.7  $\mu$ m.

#### 2. Methods

All experiments were performed under argon atmosphere. Tetrahydrofuran (THF) and dichloromethane  $(CH_2Cl_2)$  were distilled prior to use. Williamson etherification and Suzuki coupling reactions were used to obtain the chiral dopants. The chemical compounds (R)-2,2'-dihydroxy-1,1'-binaphthyl (optical purity, 0.99) and 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl were purchased from commercially available sources. The mesogenic compound 4-(trans-4-n-pentylcyclohexyl)bromobenzene [PCH5Br] was commercially available. A di-substituted binaphthyl derivative [(R)-2,2'-ethoxy-binaphthyl, abbreviatedas **D-1**] was synthesised according to the literature.<sup>12</sup> Proton (<sup>1</sup>H) nuclear magnetic resonance (NMR) spectra were measured in CDCl<sub>3</sub> using a JEOL 400 MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from tetramethylsilane as an internal standard. The chemical properties of the synthesised compounds are given in the final section. Highresolution mass spectra (HRMS) were obtained at the Technical Centre of Department of Synthetic Chemistry and Biological Chemistry of Kyoto University. The microscopic observation was performed under crossed nicols using a Carl Zeiss AXIO IMAGER MIM polarising optical microscope (POM) equipped with a Linkam TH-600PM and L-600 heating and cooling stage with temperature control. The phase transition temperatures of the S<sub>C</sub> and S<sub>C</sub><sup>\*</sup> were determined using a Perkin-Elmer differential scanning calorimeter (DSC) and a TA instrument Q100 DSC apparatus at a constant heating and cooling rate of 2 °C min<sup>-1</sup> by recording data for the first cooling and the second heating processes. X-ray diffraction (XRD) was performed using a Rigaku D-3F diffractometer equipped with a temperature

#### **Chiral dopants**



Scheme 1 Molecular structures of axially chiral binaphthyl derivatives (D-1, D-3,3', D-4,4' and D-6,6') and host liquid crystals (5CB, PhB1 and PhB2).



Scheme 2 Synthetic routes for axially chiral binaphthyl derivatives (D-3,3', D-4,4' and D-6,6').

controller under a constant heating and cooling rate of 1  $^\circ C$  min $^{-1}$ , in which X-ray power was set at 12 kW.

#### 3. Results and discussion

The binaphthyl derivatives **D-3,3'**, **D-4,4'** and **D-6,6'** were synthesised by introducing the PCH-type LC groups into the 3,3', 4,4', and 6,6' positions of the binaphthyl ring, respectively, as depicted in Scheme 1. The synthetic routes for the binaphthyl derivatives are shown in Scheme 2. Compounds **2** and **5** were synthesised according to the literature.<sup>12</sup> Note that the ethoxy group at the 2,2' positions of the binaphthyl ring remains unchanged to reduce the number of relevant parameters when evaluating the effect of chirality transcription.<sup>12</sup>

#### Chirality transfer to N-LC

N\*-LCs were prepared by adding small amounts of the binaphthyl derivatives as chiral dopants into 4-pentyl-4'-cyanobiphenyl (**5CB**) to be used as a host N-LC. All of the binaphthyl derivatives synthesised here showed good miscibility to the N-LC owing to PCH-type LC substituents. Fig. 1 shows polarised optical microscope (POM) photographs of the N\*-LCs induced by additions of 0.5 mol% D-1, D-3,3', D-4,4' and D-6,6' to 5CB. Fingerprint textures were observed in the N\*-LCs including D-3,3' (Fig. 1b) and D-6,6' (Fig. 1d). However, no fingerprint texture was found in the N\*-LCs including D-1 and D-4,4'.



**Fig. 1** Polarising optical micrographs of N\*-LCs induced by additions of 0.5 mol% of (a) **D-1**, (b) **D-3,3'**, (c) **D-4,4'** and (d) **D-6,6'** into the host N-LC of **5CB**. The photographs of (a), (b) and (c) were taken at 28 °C during the cooling processes. The photograph of (d) was taken at 30 °C during the cooling process.

 Table 1
 Specific rotation and helical twisting powers of axially chiral binaphthyl derivatives

	Specific rotation, $[\alpha]_{589}^{25}$ , (deg dm <sup>-1</sup> g <sup>-1</sup> cm <sup>3</sup> )	Helical twisting power $(\mu m^{-1})$	
D-1	+6.5	10.5	
D-3,3′	-25.3	153	
D-4,4′	+10.7	11	
D-6,6′	-24.3	154	



Fig. 2 Temperature dependence of the helical pitches in the N\*-LCs induced by the additions of 0.5 mol% of the chiral dopants (D-1, D-3,3', D-4,4' and D-6,6') into 5CB.

Nevertheless, the helical pitches of the N\*-LCs were rigorously evaluated by measuring the distance between Cano lines appearing on the surface of a wedge-type cell under a POM.<sup>12</sup> The helical pitches of the N\*-LCs with **D-1**, **D-3,3'**, **D-4,4'** and **D-6,6'** were 19.0, 1.9, 18.6 and 1.7  $\mu$ m, respectively.

It is worth noting that the PCH substituents of the binaphthyl derivative allow the binaphthyl derivative to be miscible in the host N-LC, even at high binaphthyl derivative concentrations, such as 1 mol%. The change in helical pitch (p) of the N\*-LC as a function of the mole percentage of the chiral dopant was examined. The HTP of the chiral dopant, *i.e.*, its ability to convert N-LC into N\*-LC, was evaluated using the equation



Scheme 3 Synthetic routes for 4-(3-methylpentyloxy)phenyl-4-(decy-loxy)benzoate (PhB2).

 $\text{HTP} = [(1/p)/c]_{c \to 0}$ 

where *p* is the helical pitch in  $\mu$ m and *c* is the mole fraction of the chiral dopant in the N\*-LC. The HTPs of the *n*,*n'*-substituted binaphthyl derivatives (**D-3**,**3'**, **D-4**,**4'** and **D-6**,**6'**) and that of **D-1** are summarised in Table 1. The chiral dopants **D-3**,**3'** and **D-6**,**6'** have large HTPs of 153 and 154  $\mu$ m<sup>-1</sup>, respectively, which are approximately 14 times larger than that of **D-1** (HTP = 10.5). This difference can be attributed to the more efficient chirality transfer of **D-3**,**3'** and **D-6**,**6'** to the environmental N-LC molecules through van der Waals intermolecular interactions between the PCH substituents of the chiral dopant and the cyanobiphenyl moiety of the N-LC relative to **D-1**, which has no PCH substituents.

However, **D-4,4**' showed an unexpectedly small HTP value of 11  $\mu$ m<sup>-1</sup> despite having PCH substituents; the HTP value of **D-4,4**' is almost the same as that of **D-1**, 10.5  $\mu$ m<sup>-1</sup>. To explain this result, we examined the relationship between the HTP of the chiral dopant and the dihedral angle ( $\theta$ ) of LC substituents with respect to the axis of the binaphthyl ring. The dihedral angles were estimated from the equilibrium geometries calculated using the semi-empirical AM1 method. The estimated dihedral angles in **D-3,3'**, **D-4,4'** and **D-6,6'** were 60°, 0° and 60°, respectively. Thus, when the dihedral angle changed from  $\theta = 0^{\circ}$  (**D-4,4'**) to  $\theta = 60^{\circ}$  (**D-3,3'** and **D-6,6'**), the HTP of the binaphthyl derivative changed from 11 to 153–154  $\mu$ m<sup>-1</sup>, respectively. These results indicate that the substitution positions at 3,3' and 6,6' of the



**Fig. 3** Differential scanning calorimetry (DSC) thermographs and polarising optical microscope (POM) photographs of the host  $S_C$ -LCs, **PhB1** and **PhB2**. The DSC thermographs (a) **PhB1** and (b) **PhB2** were obtained with a constant heating and cooling rate of 2 °C min<sup>-1</sup>. The POM photographs of **PhB1** (c and d) and **PhB2** (e and f) were taken during the heating and cooling processes, respectively.

binaphthyl ring promote the transfer of the axial chirality of the binaphthyl derivative to the surrounding N-LC molecules.

The temperature dependence of the helical pitches in the N\*-LCs was investigated by using the Cano wedge type cell. As shown in Fig. 2, the helical pitches of the N\*-LCs including **D-3,3'** and **D-6,6'** slightly increased with increasing temperature from 5 to 25 °C. In contrast, those of the N\*-LCs including **D-1** and **D-4,4'** showed no noticeable temperature dependence. These results suggest that the dihedral angle of the binaphthyl rings of **D-3,3'** and **D-6,6'** may become smaller owing to the increase in thermal motion of the chiral dopant, resulting in a slight decrease in helical twisting of the binaphthyl rings. The LC substituents at the 3,3' or 6,6' positions of the binaphthyl rings should amplify the sensitivity of the helical twisting to the thermal motion.

Meanwhile, the LC substituents at the 4,4' positions of the binaphthyl rings are parallel to the helical axis at the 1,1' positions and hence they do not effectively affect the twisting of the helical axis under the thermal motion. The negligibly small temperature dependence in **D-4,4'** is common to **D-1,1'**, where the large steric repulsion between hydrogens at the 8,8' positions of the binaphthyl rings restricts the internal rotation around the helical axis of 1,1' positions.<sup>12,15</sup>

#### Preparation of smectic LCs

4-(4-Methylpentyloxy)phenyl-4-(decyloxy)benzoate [abbreviated as PhB1] and 4-(3-methylpentyloxy)phenyl-4-(decyloxy)benzoate [PhB2] were synthesised to prepare S<sub>C</sub>-LCs (Scheme 3).<sup>21</sup> The mesomorphic properties of PhB1 and PhB2 were investigated using POM, DSC and XRD measurements. Fig. 3a and b show DSC data for PhB1 and PhB2, respectively. The phase transition temperatures of **PhB1** were K  $\rightarrow$  50 °C (87 J g<sup>-1</sup>)  $\rightarrow$  S<sub>X</sub>  $\rightarrow$  72 °C (0.2 J g^{-1})  $\rightarrow$  S\_A  $\rightarrow$  76 °C (15 J g^{-1})  $\rightarrow$  I and I  $\rightarrow$  73 °C  $\begin{array}{l} (18 \text{ J } \text{g}^{-1}) \rightarrow \text{S}_{\text{A}} \rightarrow 69 \ ^{\circ}\text{C} \ (0.4 \text{ J } \text{g}^{-1}) \rightarrow \text{S}_{\text{C}} \rightarrow 39 \ ^{\circ}\text{C} \ (13.1 \text{ J } \text{g}^{-1}) \\ \rightarrow \text{S}_{\text{X}} \rightarrow 6 \ ^{\circ}\text{C} \ (13.4 \text{ J } \text{g}^{-1}) \rightarrow \text{K} \text{ for the heating and cooling} \end{array}$ processes, respectively (Fig. 3a). Meanwhile, the phase transition temperatures of **PhB2** were K  $\rightarrow$  50 °C (73 J g<sup>-1</sup>)  $\rightarrow$  S<sub>A</sub>  $\rightarrow$ 62.5 °C (11 J g<sup>-1</sup>)  $\rightarrow$  I and I  $\rightarrow$  62.2 °C (11.9 J g<sup>-1</sup>)  $\rightarrow$  S<sub>A</sub>  $\rightarrow$ 12.1 °C (5.3  $J~g^{-1})$   $\rightarrow$   $S_{C}$   $\rightarrow$  5.3 °C (16.5  $J~g^{-1})$   $\rightarrow$  K for the heating and cooling processes, respectively (Fig. 3b). Here, K, S<sub>C</sub>, SA and I denote the crystal, smectic C, smectic A and isotropic phases, respectively, and the enthalpy changes associated with the phase transitions are given in parentheses. The behaviours of the LC phase transitions in PhB1 and PhB2 were of monotropic nature. POM photographs of PhB1 and PhB2 showed fan-shape textures characteristic of smectic phases at 50 °C and 40 °C in the cooling process, respectively (Fig. 3c-f).

The XRD measurement of **PhB2** was performed during the cooling process (Fig. 4a). At 55 °C, a broad diffraction peak was observed in the large-angle region ( $2\theta = 19.8^{\circ}$ ), corresponding to the LC intermolecular distance of 4.5 Å. A sharp diffraction peak in the small-angle region ( $2\theta = 2.8^{\circ}$ ) corresponds to an interlayer distance of d = 31.5 Å, which is similar to the molecular length of the **PhB2** (l = 30 Å). It follows that the LC phase of **PhB2** at 55 °C can be assigned to the smectic A (S<sub>A</sub>) phase. When cooled from 55 °C to 42 °C, the interlayer distance decreased from 31.5 to 23 Å. The *dll* ratio of 0.77 implies that the tilted structure is formed, yielding the S<sub>C</sub> phase. The tilt angle ( $\alpha$ ) defined between the layer normal and the director of LC molecules was calculated



**Fig. 4** (a) X-ray diffraction (XRD) profiles of **PhB2** measured in the cooling process. (b) Schematic illustration of the molecular arrangements in the  $S_C$  (left) and  $S_A$  (right) phases **PhB2**. *z*: Layer normal and *n*: director.

to be 40° from the equation  $\alpha = \cos^{-1}(d/l)$ . The schematic representations of the  $S_A$  and  $S_C$  phases of **PhB2** are shown in Fig. 4b.

#### Chirality transfer in S<sub>C</sub>-LCs

The binaphthyl derivatives of D-1, D-3,3', D-4,4' and D-6,6' were added as chiral dopants into the  $S_C$ -LC of PhB1. As a result, the

Table 2 Helical pitches of  $S_{\rm C}{}^{\ast}$  phases induced between host LCs and chiral dopants

Host LC	Chiral dopant		
	Type	Concentration (mol%)	Helical pitch <sup>a</sup> (µm)
PhB1	D-3,3′	1.0	4.4
	D-6,6′	0.5	4.0
	, i i i i i i i i i i i i i i i i i i i	1.0	1.6
		1.5	1.4
PhB2	D-3,3′	1.0	3.7
	D-6,6′	0.375	4.3
	, i i i i i i i i i i i i i i i i i i i	0.5	2.7
		1.0	1.4
		1.5	1.2

<sup>a</sup> Measured at 60 °C in PhB1, measured at 27 °C in PhB2.





Fig. 5 DSC thermographs and POM photographs of the host  $S_C$ -LC, PhB1 with 1 mol% of D-6,6'. The DSC thermographs (a) PhB1 with 1 mol% of D-6,6' were obtained with a heating and cooling rate of 2 °C min<sup>-1</sup>. The POM photographs of PhB1 with 1 mol% of D-6,6' were taken during the heating (b) and cooling (c) processes.

chiral dopants of **D-3**,3' and **D-6**,6' only gave rise to chiral smectic C (S<sub>C</sub>\*) phases, where the typical helical pitches were 4.4 and 1.6 µm, respectively, when 1.0 mol% chiral dopants were used (see Table 2). As shown in Fig. 5, the mesomorphic properties of **PhB1** including **D-6**,6' [abbreviated as **PhB1–D-6**,6'] were investigated in more detail by using DSC and POM measurements. The DSC thermographs of **PhB1** with 1 mol% of **D-6**,6' were obtained with heating and cooling rates of 2 °C min<sup>-1</sup>. The phase transition temperatures of **PhB1–D-6**,6' were  $K \rightarrow 50 \degree C (70.4 \text{ J g}^{-1}) \rightarrow S_X \rightarrow 60 \degree C (0.2 \text{ J g}^{-1}) \rightarrow \text{S}_C^* \rightarrow 67 \degree C (0.003 \text{ J g}^{-1}) \rightarrow \text{S}_A \rightarrow 75 \degree C (10.1 \text{ J g}^{-1}) \rightarrow \text{S}_C^* \rightarrow 55 \degree C (0.3 \text{ J g}^{-1}) \rightarrow \text{S}_{X1} \rightarrow 38 \degree C (11.2 \text{ J g}^{-1}) \rightarrow \text{S}_{X2} \rightarrow 7 \degree C (14.8 \text{ J g}^{-1}) \rightarrow \text{K}$  for the heating and cooling processes, respectively (Fig. 5a). The POM photographs of **PhB1–D-6**,6' were taken

Fig. 6 shows POM photographs of the **PhB2** including 1 mol% of **D-1**, **D-3,3'**, **D-4,4'** and **D-6,6'**, respectively. The POM photographs of **PhB2–D-1** and **PhB2–D-4,4'** showed fan-shape textures characteristic of the  $S_A$  phase at 30 °C and 50 °C during the cooling processes, respectively (Fig. 6a and c). When the chiral dopants of **D-3,3'** and **D-6,6'** were used, the striated fan-shape textures were observed at 35 °C (Fig. 6b and d).

As shown in Fig. 7a, DSC indicates that PhB2-D-6,6' has a monotropic  $S_C^*$  phase. Namely, the  $S_C^*$  phase was observed only on the cooling process. This is in contrast to the case of **PhB1–D-6,6**' with the enantiotropic  $S_C^*$  phase. The phase transition temperatures of **PhB2–D-6,6**' were K  $\rightarrow$  50 °C (78.2 J g<sup>-1</sup>)  $\rightarrow S_{X} \rightarrow 54 \ ^{\circ}C \rightarrow S_{A} \rightarrow 62 \ ^{\circ}C (9.9 \ J \ g^{-1}) \rightarrow I \text{ and } I \rightarrow 59 \ ^{\circ}C (6.0 \ J \ g^{-1}) \rightarrow S_{A} \rightarrow 29 \ ^{\circ}C \rightarrow S_{C}^{*} \rightarrow 22 \ ^{\circ}C \rightarrow S_{X1} \rightarrow 9 \ ^{\circ}C (3.4 \ J \ g^{-1}) \rightarrow S_{X2} \rightarrow 5 \ ^{\circ}C (9.7 \ J \ g^{-1}) \rightarrow K \text{ during the heating and}$ cooling processes, respectively. The phase transitions and the enthalpy changes in PhB2-D-1, PhB2-D-3,3', PhB2-D-4,4' and PhB2–D-6,6' are also shown in Fig. 8. Fig. 7b depicts the XRD patterns of PhB2-D-6,6' at 50 °C and 27 °C during the cooling process. The XRD at 50 °C exhibited a sharp diffraction peak in the small-angle region ( $2\theta = 2.7^{\circ}$ ), corresponding to an interlayer distance of d = 32.7 Å. From the XRD and POM results, the LC phase of PhB2-D-6,6' at 50 °C was assigned as the SA phase. When cooled to 27 °C, the diffraction peak was observed at an angle of 4.4° in  $2\theta$  (d = 20 Å). Moreover, a sharp diffraction peak was observed in the wide angle region at  $22^{\circ}$  in  $2\theta$ , which corresponds to the LC intermolecular distance of 4 Å (Fig. 7C). The ratio (d/l) between the interlayer distance (d) and the molecular length (l) was 0.67, suggesting that the LC molecules form a tilted structure. The tilt angle between the layer normal



Fig. 6 POM photographs of (a and c)  $S_A$  and (b and d)  $S_C^*$  phases induced by the additions of 1 mol% of (a) D-1, (b) D-3,3', (c) D-4,4' and (d) D-6,6' into the host  $S_C$ -LCs of PhB2.





Fig. 7 (a) DSC thermograph and (b) XRD profiles of **PhB2** with 1 mol% of **D-6,6**'. XRD diffractions were measured during the cooling process. (c) Schematic illustration of the molecular arrangements in the  $S_C^*$  and  $S_A$  phases.

and the director of the LC molecules was estimated to be 48°. Thus, the LC phase of **PhB2–D-6,6**′ at 27 °C was assigned as the  $S_C^*$  phase. The helical structure in the  $S_C^*$  phase is represented



**Fig. 8** The phase transition temperatures (°C) and transition enthalpies  $[\Delta H (J g^{-1})]$  (measured on cooling and heating rate of 2 °C min<sup>-1</sup>) of **PhB2–D-1**, **PhB2–D-3**,3', **PhB2–D-4**,4' and **PhB2–D-6**,6'.



Fig. 9 Changes in the helical pitch of  $S_C^*$  as a function of the mole percentage of the chiral dopant **D-6**,6' added into the host LC, **PhB1** and **PhB2**.

by a precession of the director n around the layer normal z, where the azimuth angle is kept constant (see the picture at the left side in Fig. 7c).

The helical pitch of the  $S_C^*$  phase was estimated by directly measuring the distances between the striated lines of the optical texture in POM.<sup>1,22</sup> The results are summarized in Table 2. The  $S_C^*$  phases of **PhB2** induced by the chiral dopants (1 mol%) of **D-3,3**' and **D-6,6**' showed helical pitches of 3.7 µm and 1.4 µm, respectively (see also Fig. 6b and d). Considering these results, the latter (**D-6,6**') is more promising for the transfer of the axial chirality of the binaphthyl derivative to the surrounding host LC molecules of **PhB2**. The favourableness of **D-6,6**' as the chiral dopant giving highly twisted  $S_C^*$  phase also holds for **PhB1** (Table 2).

Subsequently, the dependence of the helical pitch on the concentration of the chiral dopant was examined in the  $S_C^*$ -LCs of **PhB1–D-6,6**′ and **PhB2–D-6,6**′, for which the  $S_C^*$  temperatures at 60 and 27 °C were used, respectively. As depicted in Fig. 9, the helical pitches varied from 4.0 to 1.4 µm for mole percentages from 0.5 to 1.5 mol% for **D-6,6**′ in **PhB1**, while those from 4.3, 2.7 to 1.2 µm for mole percentages from 0.375, 0.5 to 1.5 mol% for **D-6,6**′ in **PhB2**. It is evident that **PhB2** forms a high twisted helical  $S_C^*$ -LC with less amount of **D-6,6**′ than **PhB1**. In addition, **PhB2** shows a remarkable decrease in helical pitch (increase in helical twisting) even when a small amount of chiral dopant is added, implying that **PhB2** can more easily form the induced  $S_C^*$ -LC upon the addition of the chiral dopant than **PhB1**.

Finally, it is worth noting that tilt angle ( $\theta$ ) in the S<sub>C</sub>\*-LC is estimated to be 48° as depicted in Fig. 7c, and this value is larger than that (40°) in the S<sub>C</sub>-LC (Fig. 4b). Namely, the tilt angle of the S<sub>C</sub>-LC increased by 8° when the chiral dopant, **D-6,6'** was added into the host LC, **PhB2**, to form the S<sub>C</sub>\*-LC. It is likely that, upon the addition of the chiral dopant, the LC molecules in the S<sub>C</sub> phase are rearranged by the precessing motion about the layer normal to avoid the steric repulsion incurred by the chiral dopants, generating a one-handed screwed S<sub>C</sub>\* phase. This rearrangement could be easier when the tilt angle is larger because of the larger motional spacing for the LC molecules. This remark may lead to a guideline for designing the LC molecules that can be used as the host S<sub>C</sub>-LCs producing the induced S<sub>C</sub>\* phase with an aid of the chiral dopants.

#### 4. Conclusion

We synthesised novel atropisomeric chiral inducers, axially chiral binaphthyl derivatives bearing LC groups at the n,n' positions (n = 3, 4, 6) of the binaphthyl rings. The chirality transfer from the axially chiral binaphthyl derivatives to the N-LC molecules was largely affected by the dihedral angle of LC groups with respect to the chiral axis of the binaphthyl moiety. When the LC groups were introduced at the 3,3' and 6,6' positions of the binaphthyl rings, the dihedral angle became  $60^{\circ}$ , leading to high HTPs of 153 and 154  $\mu$ m<sup>-1</sup>, respectively. In contrast, when the LC groups were substituted at the 4,4' position of the binaphthyl rings, the dihedral angle became  $0^{\circ}$ , resulting in a small HTP of  $11 \ \mu$ m<sup>-1</sup>. The substituents at the 3,3' and 6,6' positions of the binaphthyl rings are effective in the chirality transfer of the chiral dopant to the environmental N-LC molecules.

The  $S_C^*$  phases were induced when the dopant, **D-3**,3' or **D-6**,6' was added to the host LCs, **PhB1** and **PhB2**. This means that it is possible to not only induce the  $S_C^*$ -LC by using the chiral dopants and the host LCs, but also tune the helical pitch of the  $S_C^*$ -LC by choosing the combination between the chiral dopant and the host LC. In particular, the highly twisted  $S_C^*$  phases with helical pitches of 1.2–1.4 µm were prepared in **PhB1** and **PhB2** by using the chiral dopant of **D-6**,6'. The 6,6' positions of binaphthyl rings are the optimal substitution positions for achieving the chirality transfer effectively from the axially chiral binaphthyl moieties to the N- and  $S_C$ -LCs.

This comprehensive study of the optimal substitution position of axially chiral binaphthyl derivatives for effective chirality transfer might lead to the molecular designs of other atropisomers and even chiroptical materials.

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