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We demonstrated the distinct helical twist-bend nematic phase behaviors associated with the ester-bond direction in two homologous series of sulfur-linked cyanobiphenyl liquid-crystal (LC) dimers (CBCOOnSCB and CBOCOOnSCB) with different molecular bend angles. We developed both homologous series and found that the helical pitches for CBOCOOnSCB were approximately double than those of CBCOOnSCB using tender resonant X-ray scattering at the sulfur K-edge. The pitches of CBOCOOnSCB and CBCOOnSCB were longer and shorter than those of the usual LC dimers, respectively. The molecular bend (or biaxiality) of LC dimers strongly impacts the helical pitch.

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## Distinct twist-bend nematic phase behaviors associated with the ester-linkage direction of thioether-linked liquid crystal dimers†

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The twist-bend nematic phase ( $N_{TB}$ ) is a new spontaneous symmetry-breaking phenomenon observed in fluidic liquid crystal (LC) phases, which possesses a heliconical structure with a pitch ranging from several to tens of nanometers. Herein we demonstrate the distinct nano-to-macroscopic  $N_{TB}$  phase behaviors associated with the ester-bond direction in two homologous series of sulfur-containing cyanobiphenyl-based LC dimers, viz. CBCOOnSCB and CBOCO $n$ SCB ( $n = 2, 4, 6, 8,$  and  $10$ ). Both the series (excluding  $n = 2$ ) formed  $N_{TB}$  phases in which the homologues ( $n = 4$  and  $6$ ) exhibited the  $N_{TB}$  phases across a broad temperature range, which were observed to be stable even at room temperature and eventually formed  $N_{TB}$  glasses. We found that both homologues ( $n = 4$  and  $6$ ) displayed distinct phase-transition properties and optical textures with respect to the  $N_{TB}$  phases. By performing tender resonant X-ray scattering measurements at the sulfur K-edge, we discovered their distinctly different nanoscopic helical pitch lengths. Within a similar shifted temperature, the pitches for CBOCO $n$ SCB showed strong temperature dependence and were approximately double those of CBCOOnSCB, which exhibited significantly weaker temperature dependence. Compared to those of the representative twist-bend nematogenic dimers, the pitches of CBOCO $n$ SCB and CBCOOnSCB are longer and shorter, respectively. It is assumed that the molecular bend (or the molecular biaxiality) of LC dimers strongly influences the precession angle of the heliconical helix, and hence the resulting pitch. These findings provide new insights into the molecular designs to modulate the nanoscale helical pitches of the  $N_{TB}$  phases.

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## Introduction

Liquid crystals (LCs) are involved in several spontaneous symmetry-breaking phenomena associated with chirality and helices, which have been the subject of great interest in the field of molecular sciences.<sup>1–10</sup> At present, the twist-bend nematic ( $N_{TB}$ ) phase, a new helical LC phase, is a hot research topic in the field of LCs. Although the  $N_{TB}$  phase was theoretically proposed<sup>11,12</sup> and simulated in earlier works,<sup>13</sup> it has only recently been experimentally demonstrated with a bent achiral dimer.<sup>14</sup> The  $N_{TB}$  phase is believed to originate from the twist and bend deformations of bent molecules, resulting in a heliconically arranged director periodicity, wherein the local

director tilts against the helical axis. Due to this phenomenon, right- and left-handed helical nanostructures and their associated degenerate domains are observed to spontaneously form, even from achiral molecules. On the other hand, another model, named the polar-twisted nematic ( $N_{PT}$ ) phase, for the heliconical mesophase identified as the  $N_{TB}$  phase was proposed, which is under debate.<sup>15–17</sup> Macroscopic chirality of the  $N_{TB}$  phase was verified using circular dichroism spectroscopy.<sup>18</sup> Several techniques, including electro-optical measurements,<sup>19</sup> freeze-fracture transmission electron microscopy,<sup>20,21</sup> and resonant soft, hard, and tender X-ray scattering measurements,<sup>22–27</sup> suggest that the helical pitch of an  $N_{TB}$  phase formed by several molecules is  $\sim 10$  nm, which is significantly shorter than the pitch of a typical chiral N phase or cholesteric phase exhibiting a helicoidal helix (generally hundreds of nanometers). Materials that exhibit the  $N_{TB}$  phase have been employed for various LC applications, such as wavelength-tunable selective light reflection<sup>28–31</sup> and optical memory<sup>32</sup> devices, LC physical gels,<sup>33</sup> photo-switchable viscoelastic bodies,<sup>34</sup> and photoalignment technology.<sup>35</sup>

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To date, a number of bent LC dimers composed of two mesogenic structures connected with an odd-numbered oligomethylene spacer have been shown to exhibit the  $N_{TB}$  phase.<sup>36–57</sup> In addition, several LC oligomers (*e.g.*, trimers,<sup>53,58–63</sup> tetramers,<sup>58,59,64</sup> a hexamer,<sup>65</sup> and other types of oligomers<sup>66–69</sup>), polymers,<sup>70</sup> and bent-core molecules<sup>71,72</sup> have also been identified as twist-bend nematogens. It should be noted here that the bent molecular geometry is key to designing twist-bend nematogens. The angle of the molecular bend and the stability of the  $N_{TB}$  phase are highly dependent on the bonds linking the two rigid mesogenic arms and the flexible oligomethylene spacer; *e.g.*, methylene-linked cyanobiphenyl (CB)-based  $CB_nCB$  dimers (representative twist-bend nematogens)<sup>14,36,37</sup> and ether-linked  $CBO_nOCB$  dimers (conventional nematogens).<sup>73</sup> Mandle *et al.* comprehensively studied the relationship between the bend angle of several CB dimers with different linkages and their  $N_{TB}$  formation using both experimental and quantum calculation approaches.<sup>45,54</sup> In addition, the influence of various combinations of chalcogens and other linkages on the  $N_{TB}$  phase incidence and stability has been studied.<sup>52,53</sup> We previously reported<sup>53</sup> a number of systematically designed thioether-linked LC dimers to ascertain the molecular design necessary to form the  $N_{TB}$  phase; unsymmetrical ester- and thioether-linked CB-based dimers with a butylene spacer, *viz.*  $CBCOO_4SCB$  and  $CBOCO_4SCB$  (Fig. 1), formed  $N_{TB}$  phases when supercooled to room temperature to be a  $N_{TB}$  glass ( $N_{TB}G$ ). The latter displayed behaviors typically observed in twist-bend nematogens, including a second-order-like  $N-N_{TB}$  transition and clear blocky, focal conic, and striped textures. Whereas the former  $CBCOO_4SCB$  exhibited unusual behaviors such as a first-order-like  $N-N_{TB}$  transition and ambiguous striped optical textures that were extremely thin. The origin of such differences between the dimers is yet to be determined. One possibility is that these phenomena may be a consequence of the distinct helical structures present at the nanoscale due to oppositely directed ester-linkages. Evaluation of the helical pitches of a homologous series of dimers using tender resonant X-ray scattering (TRexS) at the sulfur K-edge can be one of the most helpful techniques to understand such nano-to-macroscopic structural associations.<sup>24–27</sup>

This is the first report of the synthesis, detailed phase-transition behaviors, and distinct nano-to-macroscopic  $N_{TB}$  phase behaviors associated with different helical nanostructure modes of two homologous series of sulfur-containing LC dimers with oppositely directed ester-linkages. Unsymmetrical ester- and thioether-linked CB-based dimer homologues were synthesized, *viz.*  $CBCOO_nSCB$  and  $CBOCO_nSCB$

( $n = 2–10$ , even numbers only), which contain oppositely directed esters (*i.e.*,  $-C=O-$  and  $-OC=O-$ , respectively). The number of carbon atoms in the oligomethylene spacers ( $n$ ) were selected such that the total number of atoms in the linkage and the spacer along the chain is an odd number, thereby giving an overall bent molecular geometry. We evaluated the phase transitions and mesomorphism of the dimers using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and conventional X-ray diffractometry (XRD), and analyzed the helical structures using TRexS at the sulfur K-edge.

## Results and discussion

The synthetic procedures and characterization of the homologous series of  $CBCOO_nSCB$  and  $CBOCO_nSCB$  are described in the ESI.† Their phase sequences, phase-transition temperatures at crystallization ( $T_{Cr}$ ), glass transition ( $T_g$ ),  $N-N_{TB}$  phase transition ( $T_{NNTB}$ ), isotropic (I)– $N$  phase transition ( $T_{IN}$ ), entropy changes ( $\Delta S$ ) scaled by the gas constant ( $R$ ) at the I– $N$  and  $N-N_{TB}$  phase transitions ( $\Delta S_{IN}/R$  and  $\Delta S_{NNTB}/R$ , respectively), and  $T_{NNTB}/T_{IN}$  at a cooling rate of  $10\text{ }^\circ\text{C min}^{-1}$  are summarized in Table 1. The phase-transition data obtained during the first heating are listed in Tables S1 and S2 (see ESI†).

In terms of the phase-transition behavior of the  $CBCOO_nSCB$  series, the dimers with  $n = 4, 6, 8$ , and  $10$  exhibited a monotropic  $N_{TB}$  phase below the  $N$  phase, whereas the shortest  $CBCOO_2SCB$  dimer exhibited only a monotropic  $N$  phase. The monotropic  $N$  phase of  $CBCOO_2SCB$  appeared at  $83\text{ }^\circ\text{C}$  and was partially supercooled to room temperature upon cooling. This  $N$  phase could only be observed using POM due to crystallization of the dimer (Fig. S1 and S9, ESI†).  $CBCOO_6SCB$  and  $CBCOO_8SCB$  displayed transitions to the  $N_{TB}$  phase from the corresponding  $N$  phase at  $75$  and  $85\text{ }^\circ\text{C}$ , respectively. Notably,  $CBCOO_6SCB$  exhibited the  $N_{TB}$  phase across a broad temperature range, which was supercooled to room temperature and ultimately underwent vitrification to form a  $N_{TB}G$ , similar to  $CBCOO_4SCB$ .<sup>53</sup> The DSC curves of  $CBCOO_6SCB$  are shown in Fig. 2(a). The  $N-N_{TB}$  phase-transition peak was identified as a first-order-like transition with a  $\Delta S_{NNTB}/R$  value of  $0.54$ , which differs from the second-order-like transition behavior typically observed for twist-bend nematogens. The  $N_{TB}$  phase of  $CBCOO_8SCB$  crystallized at  $76\text{ }^\circ\text{C}$  and the dimer bearing the longest spacer (*i.e.*,  $CBCOO_{10}SCB$ ) also exhibited the  $N_{TB}$  phase, but underwent crystallization at approximately  $90\text{ }^\circ\text{C}$ , as can be seen from the DSC curves (Fig. S11 and S12, ESI†); the  $N_{TB}$  phases could be



Fig. 1 Molecular structures of  $CBCOO_nSCB$  ( $n = 2, 4, 6, 8$ , and  $10$ ) and  $CBOCO_nSCB$  ( $n = 2, 4, 6, 8$ , and  $10$ ), where  $n = 2m$ .



**Table 1** Phase sequences, transition temperatures (°C), and entropy changes scaled by the gas constant ( $\Delta S/R$ ) of CBCOO $n$ SCB and CBOCO $n$ SCB upon cooling

$n$ (CBCOO $n$ SCB)		$T_{Cr}$ (°C)	$\Delta S_{Cr}/R$		$T_{NNTB}$ (°C)	$\Delta S_{NNTB}/R$		$T_{IN}$ (°C)	$\Delta S_{IN}/R$		$T_{NNTB}/T_{IN}$
2	Cr	129.0	11.8	—	—	—	—	83 <sup>a</sup>	—	I	—
4	G	20.7	—	N <sub>TB</sub>	52.3	0.18	N	68.7	0.02	I	0.95
6	G	22.3	—	N <sub>TB</sub>	75.4	0.54	N	87.1	0.09	I	0.97
8	Cr	75.8	12.6	N <sub>TB</sub>	85 <sup>a</sup>	—	N	99.0	0.30	I	0.96
10	Cr	90.3	12.1	N <sub>TB</sub>	87 <sup>a</sup>	—	N	104.9	0.40	I	0.95
$n$ (CBOCO $n$ SCB)											
2	Cr	131.0	10.1	—	—	—	N	134 <sup>a</sup>	—	I	—
4	G	17.5	—	N <sub>TB</sub>	82.3	—	N	150.0	0.46	I	0.84
6	G	14.3	—	N <sub>TB</sub>	94.9	—	N	149.0	0.57	I	0.87
8	Cr	78.7	10.7	N <sub>TB</sub>	93 <sup>a</sup>	—	N	145.4	0.84	I	0.87
10	Cr	97.4	10.9	N <sub>TB</sub>	91 <sup>a</sup>	—	N	140.6	1.11	I	0.88

<sup>a</sup> Determined by POM.**Fig. 2** DSC curves of (a) CBCOO6SCB and (b) CBOCO6SCB recorded at a rate of 10 °C min<sup>-1</sup>.

observed only in small supercooled N domains using POM (Fig. S3, S5, S7 and S8, ESI<sup>†</sup>).

Regarding the phase-transition behavior of the CBOCO $n$ SCB series, dimers with  $n = 4, 6, 8,$  and  $10$  formed a monotropic N<sub>TB</sub> phase below the N phase temperature. Like CBCOO2SCB, the dimer with the shortest spacer (CBOCO2SCB) only formed the monotropic N phase. The N phase of CBOCO2SCB was very narrow, which could be observed by POM but was not detected by DSC due to crystallization during cooling (Fig. S6 and S13, ESI<sup>†</sup>). As shown in Fig. 2(b), CBOCO6SCB exhibited a remarkably stable N<sub>TB</sub> phase when supercooled to room temperature, with vitrification taking place at 14 °C to form the N<sub>TB</sub>G phase;

this behavior is similar to that of CBOCO4SCB.<sup>53</sup> Furthermore, the N–N<sub>TB</sub> phase transition at 94.9 °C is similar to the second-order-like phase-transition typically observed for the majority of twist-bend nematogens. CBOCO8SCB exhibited the N<sub>TB</sub> phase at temperatures ranging from 93 to 79 °C, below which it underwent crystallization. The N–N<sub>TB</sub> phase transition at 85 °C could not be detected by DSC due to crystallization (Fig. S16, ESI<sup>†</sup>). Moreover, the N<sub>TB</sub> phase was observed only in the supercooled N domains of CBOCO10SCB; hence, no N–N<sub>TB</sub> transition peak could be detected *via* DSC (Fig. S8 and S17, ESI<sup>†</sup>). Unlike CBCOO $n$ SCB, which exhibited monotropic mesophases, CBOCO $n$ SCB with  $n = 4, 6, 8,$  and  $10$  gave rise to enantiotropic N phases. In addition, the above-mentioned observations indicate that mid-length spacers ( $n = 4$  and  $6$ ) of both homologous series enhanced the N<sub>TB</sub> phase ranges, which ultimately resulted in the formation of a room-temperature N<sub>TB</sub> phase or N<sub>TB</sub>G phase.

The  $T_{IN}$ ,  $T_{NNTB}$ , and  $\Delta S_{IN}/R$  values as a function of  $n$  for CBCOO $n$ SCB and CBOCO $n$ SCB ( $n = 4, 6, 8,$  and  $10$ ) are displayed in Fig. 3. The phase-transition temperatures are higher for CBOCO $n$ SCB than for CBCOO $n$ SCB, except  $T_g$ . This difference can be attributed primarily to their different geometries according to the all-*trans* model of spacer chains; in other words, their molecular biaxiality and shape anisotropy. The inter-arm bend angle ( $\alpha$ ) between the *para*-axes of the two mesogenic arms of CBCOO4SCB ( $\alpha = 105^\circ$ ) is significantly smaller than that of CBOCO4SCB ( $\alpha = 127^\circ$ ).<sup>53</sup> This difference is caused by the opposed ester-bond directions or the different positions of carbonyl (C=O) and –O–C– bonds in the esters. Notably, the  $T_{IN}$  values of CBCOO $n$ SCB were found to strongly depend on  $n$ , whereas those of CBOCO $n$ SCB were only slightly affected by  $n$ . The  $T_{NNTB}$  values of CBCOO $n$ SCB sharply decreased with a decrease in  $n$ , while the corresponding values of CBOCO $n$ SCB did not. It is worth noting that the  $\Delta S_{IN}/R$  values are significantly smaller for CBCOO $n$ SCB than for CBOCO $n$ SCB. The abovementioned trends may be associated with the more bent geometry of CBCOO $n$ SCB with the smaller bend angle or the more anisotropic geometry of CBOCO $n$ SCB.<sup>48</sup> The  $\Delta S_{IN}/R$  values of both homologous series were found to gradually decrease with decreasing  $n$ , which can be ascribed to the molecular structural biaxiality that is enhanced by





Fig. 3 (a)  $T_{IN}$ , (b)  $T_{NNTB}$ , and (c)  $\Delta S_{IN}/R$  values as a function of  $n$  for  $CBCOOnSCB$  with  $n = 4, 6, 8,$  and  $10$  (red circles) and  $CBOCOOnSCB$  with  $n = 4, 6, 8,$  and  $10$  (blue squares).

decreasing the spacer length, thereby reducing molecular anisotropy. In addition, the reduced temperature,  $T_{NNTB}/T_{IN}$ , values for  $CBOCOOnSCB$  ( $\sim 0.86$ ) were smaller than those for  $CBCOOnSCB$  ( $\sim 0.96$ ), and these values remained nearly constant within each homologous series. This reflects that the  $N$ - $N_{TB}$  phase of  $CBOCOOnSCB$  originates from the supercooled  $N$  phases, which undergo a greater degree of supercooling than those of  $CBCOOnSCB$ . These trends can also be reasonably associated with their molecular geometry or anisotropy. More bent molecules can effectively form the  $N_{TB}$  phase, whereas more linear molecules typically favor formation of the conventional  $N$  phase. Hence, appearance of the  $N_{TB}$  phase for  $CBOCOOnSCB$  is naturally induced from the more supercooled  $N$  phase, resulting in lower  $T_{NNTB}/T_{IN}$  values.<sup>56</sup>

Using POM, we observed different optical textural behaviors in the  $N_{TB}$  phases for each homologous series when  $n = 4$  and  $6$ . In non-treated glass cells,  $CBCOOnSCB$  ( $n = 4$  and  $6$ ) exhibited focal conic textures (Fig. S2, ESI<sup>†</sup>),<sup>53</sup> which are typical of the  $N_{TB}$  phase. In addition, they displayed textures characterized by an elastic behavior (Fig. S2, ESI<sup>†</sup>); these textures could be recovered even when expansion took place through pressing and shearing. In our previous report,<sup>53</sup> we noted that  $CBCOO4SCB$  exhibited unusual striped texture with an obscure thinner-striped texture as shown in Fig. 4(a) using POM with a uniaxially rubbed planar cell. In this study, we conducted further POM analyses of  $CBOCO4SCB$ ,  $CBOCO6SCB$ ,  $CBCOO6SCB$ , and  $CBCOO8SCB$  using  $5 \mu\text{m}$ -thick uniaxially rubbed polyimide-surface-treated planar alignment cells. We found that  $CBOCO4SCB$  exhibited the usual optical texture of the  $N_{TB}$  phase with clear stripes [Fig. 4(c)], which is distinct from the obscure thin stripes found in  $CBCOO4SCB$  [Fig. 4(a)]. The two dimers with  $n = 6$  also displayed clearly different optical texture behaviors:  $CBCOO6SCB$  exhibited a distinct thinner-striped texture [Fig. 4(b)]; however,  $CBOCO6SCB$  displayed a more typical striped texture [Fig. 4(d)]. These were similar to the different texture behaviors of  $CBCOO4SCB$  and  $CBOCO4SCB$ . Meanwhile,  $CBCOO8SCB$  exhibited a conventional striped texture that was similar to those of the typical twist-bend nematogens and the oppositely directed esters,  $CBOCO4SCB$  and  $CBOCO6SCB$  (Fig. S4, ESI<sup>†</sup>). It seems that the unusual textures with thinner stripes observed for  $CBCOOnSCB$  were changed to the typical ones with increasing length of the central spacer. In addition to the properties associated with the first and second order phase-transitions of the  $N_{TB}$  phases of  $CBCOOnSCB$  and  $CBOCOOnSCB$  ( $n = 4$  and  $6$ ), respectively, the observed textural patterns inspired us to study the helical structures of the  $N_{TB}$  phases by means of comprehensive X-ray techniques, since previous studies suggested the presence of helical structures<sup>19–27</sup> and pseudo-layer nature in the  $N_{TB}$  phase.<sup>74,75</sup>

To analyze the structures of the observed mesophases, we firstly conducted conventional XRD measurements for both homologous series with  $n = 4$  and  $6$  (Fig. S18–S21, ESI<sup>†</sup>). In both the  $N$  and  $N_{TB}$  phases, broadened diffraction peaks were observed in the small- and wide-angle regions. These results suggest that there is no apparent positional order along the long molecular axis, and liquid-like correlations exist among lateral molecules, thereby indicating the nature of the  $N$  phase. In addition, the small-angle diffraction pattern corresponds to pseudo-layered structures that originate from the smectic ( $Sm$ )-like or cybotactic molecular clusters in the  $N$  and  $N_{TB}$  phases. The pseudo-layer lengths in the  $N_{TB}$  phase were estimated to be similar:  $1.15 \text{ nm}$  ( $2\theta = 7.6^\circ$ ) for  $CBCOO4SCB$ ,  $1.27 \text{ nm}$  ( $2\theta = 6.9^\circ$ ) for  $CBCOO6SCB$ , and  $1.32 \text{ nm}$  ( $2\theta = 6.7^\circ$ ) for  $CBOCO6SCB$  in each  $N$  phase. The intensity of the small-angle diffraction was weaker in the  $N_{TB}$  phase than in the  $N$  phase, and the  $2\theta$  values (or the pseudo-layer lengths) were temperature-independent over the entire  $N_{TB}$  phase range, which is typical of  $N_{TB}$  phases. In the case of  $CBOCO4SCB$ , the small-angle diffraction could





Fig. 4 POM images of the  $N_{TB}$  phases of (a) CBCOO4SCB, (b) CBCOO6SCB, (c) CBOCO4SCB, and (d) CBOCO6SCB in a uniaxially rubbed cell with planar alignment. The POM image in panel (a) is reproduced from ref. 53 with permission from Elsevier.

only be detected in the N phase, disappearing after transition to the  $N_{TB}$  phase (Fig. S20, ESI<sup>†</sup>).

We performed TRexS measurements at the sulfur K-edge to determine the helical pitch in the  $N_{TB}$  phases of CBCOO $n$ SCB and CBOCO $n$ SCB ( $n = 4$  and 6). TRexS at the sulfur K-edge enables the detection of resonant scattering that corresponds to the helical pitch in the  $N_{TB}$  phase, owing to the periodically distributed bond direction (rather than the conventional electron density modulation) in helical structures.<sup>24–27</sup> The two-dimensional (2D) and one-dimensional (1D) resonant X-ray scattering patterns obtained from the helical pitch periodicity in the  $N_{TB}$  phase of CBCOO4SCB are shown as representative images in Fig. 5. These scattering patterns appeared at temperatures below the N phase upon cooling and disappeared

upon re-entering the N phase upon reheating. The 2D scattering images of the other dimers and the corresponding 1D patterns are shown in Fig. S22–S27 (ESI<sup>†</sup>). Fig. 6(a) shows the temperature dependence of the helical pitch in the  $N_{TB}$  phase for both the homologous series ( $n = 4$  and 6) as a function of the shifted temperature ( $\Delta T = T_{NNTB} - T$ ). The helical pitch lengths ( $p_h$ ) were calculated from the wavenumber  $q = 2\pi/p_h$ . Upon decreasing the temperature, the  $p_h$  values decreased from 8.1 to 6.8 nm for CBCOO4SCB and from 9.3 to 7.4 nm for CBCOO6SCB, while those of CBOCO4SCB and CBOCO6SCB decreased from 20.3 to 11.9 nm and from 24.4 to 13.8 nm, respectively. Compared with those of CBOCO4SCB and CBOCO6SCB, the helical pitches of CBCOO4SCB and CBCOO6SCB were not only significantly shorter but also less temperature-dependent. The helical pitch lengths of

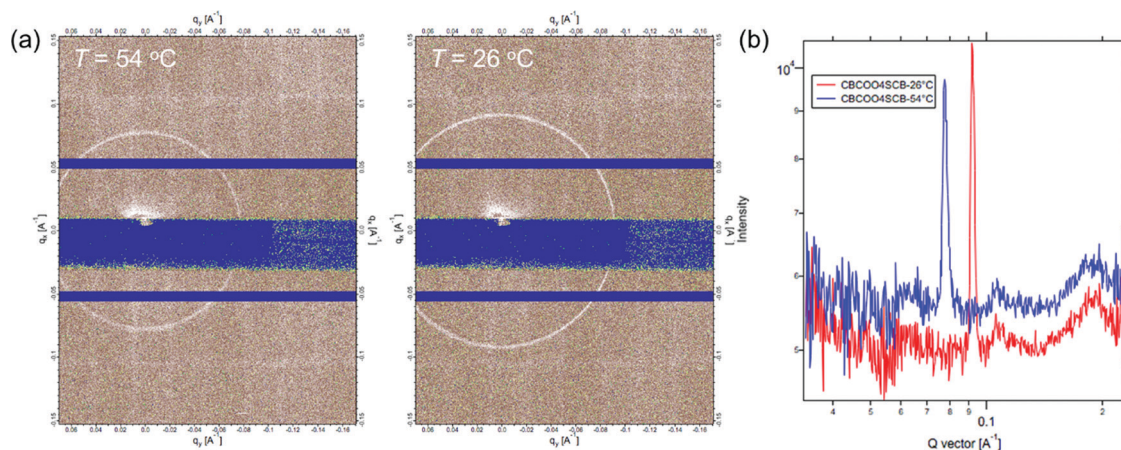


Fig. 5 (a) Typical 2D-scattered patterns and (b) the corresponding 1D patterns in the  $N_{TB}$  phase of CBCOO4SCB. Note the horizontal blue streaks in (a) are areas with no data, either due to gaps between detector modules or the beam stop used to block the direct X-ray beam.



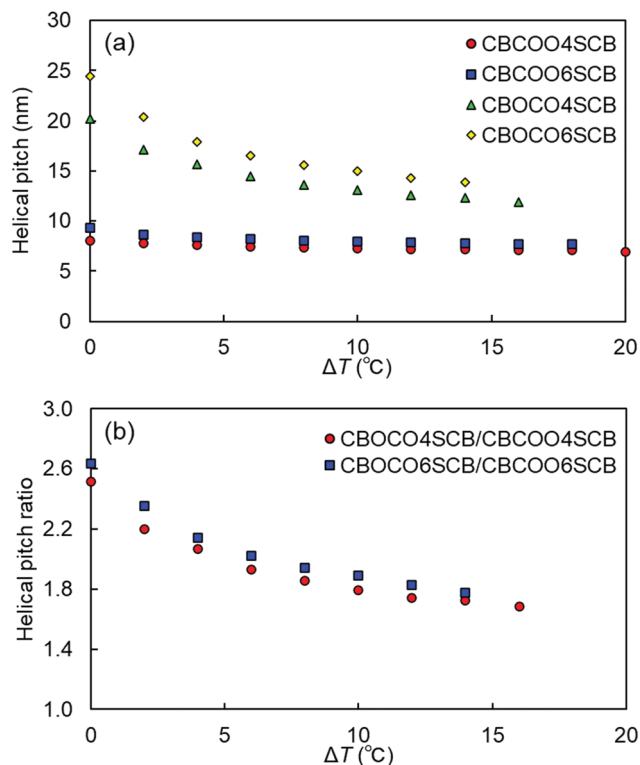


Fig. 6 (a) Helical pitches of CBCOO4SCB, CBCOO6SCB, CBOCO4SCB, and CBOCO6SCB, and (b) helical pitch ratios of CBOCO4SCB/CBCOO4SCB and CBOCO6SCB/CBCOO6SCB as a function of the shifted temperature ( $\Delta T = T_{\text{NNTB}} - T$ ).

CBOCO4SCB and CBOCO6SCB decreased upon lowering the temperature, as is typical for  $N_{\text{TB}}$  phases; this temperature

dependence may be attributed to the lower number of twisted molecular conformations (or an increase in straightened conformers)<sup>76</sup> and fluctuations in the unwinding process related to helical ordering at high temperatures, which relate to decreased precession of the molecules in the helices at high temperatures. However, the helical pitch lengths of CBCOO4SCB and CBCOO6SCB do not vary significantly at different temperatures. Furthermore, it is noteworthy that the  $p_h$  ratios of  $p_h(\text{CBOCO4SCB})/p_h(\text{CBCOO4SCB})$  and  $p_h(\text{CBOCO6SCB})/p_h(\text{CBCOO6SCB})$  are close to 2, *i.e.*, the helical pitch lengths of CBOCO $n$ SCB ( $n = 4$  and 6) were twice those of CBCOO $n$ SCB ( $n = 4$  and 6), as shown in Fig. 6(b). Density functional theory (DFT) calculations using Gaussian 16 at the B3LYP 26/6-31G(d) level of theory show that the difference in the overall molecular lengths of CBCOO4SCB (2.56 nm) and CBOCO4SCB (2.78 nm) is small; therefore, the considerable difference in their helical pitches cannot be qualitatively accounted for by the molecular lengths, which will be discussed later.

The helical pitch length is associated with the tilt angle from the helical axis ( $\theta$ ), molecular length ( $L$ ), and molecular number per turn ( $n_m$ ) (see Fig. 7);  $p_h = n_m L \cos \theta$ , and hence  $n_m$  can be estimated by calculating the value of  $2\pi/qL \cos \theta$ . With decreasing temperature, the  $\theta$  values for LC dimers typically increase by 10 to 35°.<sup>23,26,77–81</sup> Nevertheless, it is realistically assumed that  $\theta$  does not significantly influence the  $n_m$  values within the helical region. In the low temperature region of the  $N_{\text{TB}}$  phase, the  $n_m$  values were estimated as  $n_m = 3\text{--}4$  for CBCOO4SCB and CBCOO6SCB and  $n_m = 5\text{--}6$  for CBOCO4SCB and CBOCO6SCB within a similar  $\Delta T$  region.

Next, the helical models of the dimers were considered based on XRD and TRexS. The azimuthal precession ( $\varphi$ ) per



Fig. 7 Plausible helical helix models in the  $N_{\text{TB}}$  phases of (a) CBCOO4SCB and CBCOO6SCB, and of (b) CBOCO4SCB and CBOCO6SCB.



pseudo-layer was estimated from the following equation:  $\Delta\varphi = 360^\circ \times (\text{pseudo-layer length on XRD})/(p_h \text{ on TRexS})$ ; this can be used to elucidate the helical models by utilizing the polygon models.<sup>61</sup> The  $\varphi$  values were estimated to be  $\sim 60^\circ$  in the  $N_{TB}$  phase of CBCOO $n$ SCB ( $n = 4$  and  $6$ ). These  $\varphi$  values indicate a hexagonal model separated by pseudo-layers for the  $N_{TB}$  phase of CBCOO $n$ SCB ( $n = 4$  and  $6$ ). On the other hand, the  $\varphi$  values of CBOCO $n$ SCB ( $n = 4$  and  $6$ ) essentially became smaller (approximately  $30\text{--}40^\circ$ ) within the tested temperatures or led to the formation of larger polygonal structures such as a decagon due to their abnormally long helical pitches. The  $\varphi$  values of CBOCO4SCB were estimated using the pseudo-layer length in the N phase since the pseudo-layer peak almost disappeared below the  $N_{TB}$  phase.

Using the values of  $n_m$  and  $\Delta\varphi$ , we constructed two helical models in the  $N_{TB}$  phases of CBCOO $n$ SCB and CBOCO $n$ SCB ( $n = 4$  and  $6$ ). Fig. 7(a) and (b) illustrate plausible helical models with  $n_m = 3\text{--}4$  and  $\Delta\varphi = 60^\circ$  for a hexagon model of CBCOO $n$ SCB ( $n = 4$  and  $6$ ) and with  $n_m = 6\text{--}7$  for CBOCO $n$ SCB ( $n = 4$  and  $6$ ), respectively. Considering the strong temperature dependence of the helical pitches in the latter, it is assumed that the bent conformation and the stacking extent of the rigid CB arms among the dimers may also be influenced by temperature, changing the precession angles.

As described in the Introduction, the  $p_h$  values of the  $N_{TB}$  phase are  $\sim 10$  nm,<sup>19–27</sup> corresponding to several dimers. For example, the  $p_h$  of CB7CB, which is a representative twist-bend nematogen structurally analogous to CBCOO $n$ SCB and CBOCO $n$ SCB dimers, has been found to vary between 8 and 10 nm depending on the temperature.<sup>22</sup> However, the  $p_h$  values of both CBCOO $n$ SCB ( $n = 4$  and  $6$ ) were found to be somewhat smaller than those of CB7CB, while those of CBOCO $n$ SCB ( $n = 4$  and  $6$ ) were larger. That is, the oppositely directed esters caused unique and distinct helical structural modes in the  $N_{TB}$  phases of these dimers which differ from those of the typical dimer. CBCOO $n$ SCB ( $\alpha = 105^\circ$ ) can be bent to a higher extent than CBOCO $n$ SCB ( $\alpha = 127^\circ$ ), which are ascribed to the opposed ester-bond directions or the different positions of carbonyl (C=O) and –O–C– bonds in the two type esters.<sup>53</sup> In addition, the linkage point between CB and –COO– of CBCOO $n$ SCB is more rigid than that between CB and OCO CBOCO $n$ SCB. The rotational barrier of the –C(Ar)–C= bond in CBCOO $n$ SCB is higher than that of the –C(Ar)–O– bond in CBOCO $n$ SCB.<sup>82–85</sup> Thus, the increased bending and more rigid structure of CBCOO $n$ SCB should result in shorter helical pitches and a weaker temperature dependence, as compared with those of CBOCO $n$ SCB and the other reported twist-bend nematogenic dimers. This can be associated with the first-order-like  $N\text{--}N_{TB}$  transition peak that corresponds to the changes in the phase structure.

The main factor responsible for the longer helical pitch of CBOCO $n$ SCB (*i.e.*, approximately 10–25 nm) as compared to that of CB7CB (8–10 nm) is likely to be the molecular bend (or the molecular biaxiality) and the resulting precession angles of the helices. The molecular bend angle of CB $n$ CB is estimated

as  $111^\circ$  based on its all-*trans* model,<sup>45</sup> leading to a more bent geometry for CB $n$ CB than for CBOCO $n$ SCB ( $127^\circ$ ).<sup>53</sup>

On the other hand, the  $p_h$  values of both ester homologous series were marginally shorter in homologues with  $n = 4$  than those with  $n = 6$ , due to the different lengths of flexible spacer chains. As illustrated in Fig. 6, the temperature dependence of the  $p_h$  values remained essentially unchanged for both the systems.

Finally, we estimated the correlation lengths of the helices and the number of the helical stacks in the  $N_{TB}$  phases of CBCOO $n$ SCB and CBOCO $n$ SCB ( $n = 4$  and  $6$ ). Using the full width at half maximum (FWHM) of the Lorentzian fitting (FWHM =  $2/\xi$ , where  $\xi$  is the Lorentzian length) applied to the TRexS data, the Scherrer equation ( $\tau = 2\pi/\text{FWHM}$ ; wherein the shape factor is set to unity) can be used to estimate the longitudinal helical correlation or domain size.<sup>23</sup> In addition, the number of helical stacks was estimated by calculating  $\tau/p_h$ . The longitudinal correlation lengths and helical stacks are plotted as a function of  $\Delta T$ , as shown in Fig. 8. The  $\tau$  values tend to slightly increase initially with decreasing temperature in the higher  $N_{TB}$  temperature region, immediately below the N phase. This initial increase in  $\tau$  is attributable to heat fluctuations that occur close to the fluidic N phase, such that  $\tau$  becomes larger. It is interesting to note that the correlation lengths and the resulting number of the helical stacks of CBCOO $n$ SCB are calculated to be more than twice the corresponding values of CBOCO $n$ SCB (Fig. 8). These larger correlation lengths of the helices of CBCOO $n$ SCB as compared to those of CBOCO $n$ SCB are reasonable, considering



Fig. 8 (a) Correlation length (Å) and (b) helical stacks based on TRexS data scanned at 2471 eV.

their rigid molecular structures and approximately temperature-independent helical behavior, which are reminiscent of rigid packing. The helical pitches and correlation lengths of CBCOOnSCB are also essentially temperature-independent; and the estimated helical stacks naturally display a similar behavior. On the other hand, since the helical pitches of CBOCOOnSCB typically depend on temperature, the helical stacks increase with decreasing temperature.

## Conclusions

We herein reported the development of two homologous series of unsymmetrical ester- and thioether-linked cyanobiphenyl-based LC dimers, *viz.* CBCOOnSCB and CBOCOOnSCB ( $n = 2, 4, 6, 8,$  and  $10$ ). We observed that all the dimers were mesogenic, and that CBCOOnSCB and CBOCOOnSCB ( $n = 4, 6, 8,$  and  $10$ ) formed  $N_{TB}$  phases. In particular, CBCOOnSCB and CBOCOOnSCB ( $n = 4$  and  $6$ ) exhibited the  $N_{TB}$  phase across a wide temperature range. These phases were stable down to room temperature and eventually formed  $N_{TB}$  glasses. The phase-transition temperatures (excluding glass transition temperatures), and associated enthalpy and entropy changes were mostly lower for CBCOOnSCB than those observed for CBOCOOnSCB. In addition, CBCOOnSCB and CBOCOOnSCB ( $n = 4$  and  $6$ ) displayed different phase-transition properties and striped optical textures. Finally, their distinct helical structures were elucidated using TRexS measurements at the sulfur K-edge. Compared with those of the typical twist-bend nematogenic dimers, CBCOOnSCB ( $n = 4$  and  $6$ ) exhibited smaller pitch lengths with weaker temperature dependence, whereas CBOCOOnSCB ( $n = 4$  and  $6$ ) exhibited greater helical pitch lengths. The difference is ascribed to the molecular bend (or the molecular biaxiality) and structural rigidity. This study therefore provides new insights into the influence of molecular design in the  $N_{TB}$  phase, revealing that subtle structural modifications (*i.e.*, oppositely directed esters) crucially impact helical nanostructures in the  $N_{TB}$  phase.

## Experimental section

The synthetic scheme and procedures and characterization data for CBCOOnSCB and CBOCOOnSCB are described in the ESI.† The molecules were purified using column chromatography on silica gel and recrystallization.  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy were recorded on a JNM-ECS400 (400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ ) or a JNM-ECX500 (500 MHz for  $^1\text{H}$  NMR and 126 MHz for  $^{13}\text{C}$  NMR) (JEOL Ltd, Tokyo Japan). Fourier transform infrared spectroscopy (FTIR) were performed by the KBr (purchased from FUJIFILM Wako Pure Chemical Co.) method using a JASCO FT/IR-4200. High-resolution mass spectrometry (HRMS) using high-performance liquid chromatography (HPLC) (Agilent 1200 HPLC-Chip and 6520 Accurate-Mass Q-TOF) was conducted. Phase-transition behavior was studied based on POM with an Olympus (Tokyo, Japan) polarized optical microscope (BX50) with a Linkam (Surrey, UK) temperature controller LK-600PM

and differential scanning calorimetry (DSC) with a Shimadzu (Kyoto, Japan) DSC 60 at a rate of  $10\text{ }^\circ\text{C min}^{-1}$  under a flow of nitrogen gas ( $50\text{ mL min}^{-1}$ ). The POM images and DSC results for all the compounds are shown in the main text or ESI.† X-ray diffraction (XRD) measurements were conducted using a Bruker D8 DISCOVER equipped with a Vantec-500 detector using Cu-K $_{\alpha}$  radiation. The specimens, kept in capillary glass tubes of 1.5 mm diameter (purchased from WJM-Glass Müller GmbH), were aligned under a magnetic field ( $B = 300\text{ mT}$ ). According to the literature,<sup>25</sup> TRexS measurement was performed at the beamline 5.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The X-ray beam energy was tuned around the S K-edge, 2472 eV, with a channel cut double-bounce silicon (111) monochromator. A two-dimensional (2D) Pilatus detector (300 K, Dectris, Inc.) was used to collect the scattering patterns, which were subsequently converted to one-dimensional line profiles using the Nika software package.<sup>86</sup> The scattering patterns were viewed with the Xi-Cam interface<sup>87</sup> at the beamline. The sample-detector distance was tuned between 488 mm and 250 mm to access relevant  $q$  range. The beam centers and the sample-to-detector distances were calibrated using both silver behenate and 8CB.

## Conflicts of interest

There are no conflicts to declare.

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