Nanoconfined heliconical structure of twist-bend nematic liquid crystal phase

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ABSTRACT

We produced controlled heliconical structures of a twist-bend nematic (NTB) liquid-crystal (LC) phase in nanoconfinement in a porous anodic aluminium oxide (AAO) film. The structural parameters of the NTB phase such as conical angle and helical pitch can be modulated by varying the surface energy of the inner surface of the porous AAO film, done by using different self- assembled monolayers (SAMs). The LC molecules tend to be more freely packed, thus forming a larger conical angle, when placed on the tri-deca-fluoro-1,1,2,2-tetrahydrooctyl-trichlorosilane (FOTS)-treated substrate, which has a relatively low surface energy. In contrast, the molecules form a more tightly packed structure, and thus a smaller conical angle, when placed on the

2-(methoxy(polyethyleneoxy)-propyl)trimethoxysilane (PEG 6/9)-treated substrate, which has higher surface energy. This work improves our collective understanding of self-assembled heli- conical structures in the NTB phase.

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1. Introduction

Recently, bent molecules have attracted much attention in the field of soft matter owing to their chirality, strong polarisation, elastic behaviour and high flexoe- lectricity [1–4], making them useful in various applica- tions such as opto-electronic [5,6] and energy harvesting devices [2]. Because of their unique shapes, bent molecules can easily form chiral liquid-crystal (LC) structures including chiral smectic [7,8] and twist-bend nematic (NTB) phases [9–13]. In particular, the NTB phase has been a focus of interest because it

that exhibit a rapid response time in display applica- tions [15].

In the NTB phase, the LC molecules are spontaneously subjected to twist-bend deformation through a long axis (H) of the heliconical structure owing to its low bend elastic constant (K3) (Figure 1(a)) [9,12,13]. Considering a twist-bend helix along the z-direction, its local molecular director n can be expressed as: nðzÞ ¼

ðsin θ cos ψ; sin θ cos ψ; cos θÞ where Θ is the tilted con- ical angle of $0 < \theta < \pi=2$ and where ψðzÞ ¼ $2\pi z=P$ repre- sents the azimuthal angle [12,13]. Here, P is the helical

pitch of the heliconical structure. It has been reported that

has hierarchically assembled heliconical structures [14]

the NTB

phase has a fine pitch ~ 8–11 nm, and the

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Figure 1. (Colour online) NTB phase, liquid crystal molecules and experimental scheme. (a) The heliconical structure in the NTB phase. Θ is the conical angle, ψ is the azimuthal angle, n is the molecular director, H is the average director and P is the helical pitch. (b) The molecular structure of CB7CB and its thermal phase transition. (c) The anodic aluminum oxide nanochannel, where DP is the pore diameter. Here, the DP is 100 nm. (d) The schematic of filled AAO with LC molecules.

macroscopic arrangement of these heliconical structures leads to the coexistence of left- and right-handed chiral domains owing to the absence of a chiral centre. These characteristics can be confirmed by 2H NMR spectroscopy [16,17], X-ray scattering [18], the electro-clinic effect [19,20] and freeze-fracture transmission electron micro- scopy [12,13,21]. However, the key parameters that define the heliconical structure of the NTB phase at the nanometre scale are not yet clearly understood. Thus, the complexity of the heliconical NTB structure must be simplified or minimised to deeply analyse the inherent structural prop- erties of the phase. For example, the orientation of the helical axis H is difficult to control individually. Nonetheless, there have been attempts to exploit strong external electric or magnetic fields because of the structural undulation that results from the diverging helical axis, which induces spontaneous splay deformation [10,11,22,23].

In this study, we use nanoscale-topographic confine- ment to align LC molecules to produce a well-controlled NTB phase, which can minimise splay deformation of the helical axis. Topographic confinement has proven to be a powerful method to control the ordering and orientation of various LC phases [24–31]. For this investigation, a porous anodic aluminium oxide (AAO) film is synthe- sised and modified by different self-assembled mono- layers (SAMs) to control the surface anchoring on the inner surface of the AAO nanochannels [26–28]. As a result, we can produce one-dimensionally aligned helico- nical structures of the NTB phase and modulate the heli- conical packing by changing the affinity between the surface and LC molecules. This arrangement was

observed using grazing incidence X-ray diffraction

(GIXD) with synchrotron radiation.

2. Experimental part

Sample preparation

High-purity annealed (99.99%) aluminium (Al) foil (Alfa Aesar, Tewksbury, MA,USA) was electropolished in a mixture of perchloric acid and ethanol (volume ratio of 1:5) at 20 V and 3°C, and then anodised in

0.3 M oxalic acid at 40 V and 10°C. Irregular AAO nanochannels were chemically etched in the phospho- ric acid (6 wt. %) and chromic acid (1.8 wt. %) at 60°C, which results in a pre-patterned Al foil. The second anodisation was done under the same conditions, and the pore diameter was controlled by pore-widening in

0.1 M phosphoric acid at 38°C. The glass substrates were washed with acetone and ethanol, and then sev- eral times with deionised water, to remove impurities. The surface of the glasses and AAOs were chemically modified by silanisation using tri-deca-fluoro-1,1,2,2- tetrahydrooctyl-trichlorosilane (FOTS) and 2-(methoxy (polyethylenoxy)-propyl)trimethoxysilane (PEG 6/9) molecules (Gelest, Morrisville, PA, USA). Before che- mical treatment, the surfaces were treated with oxygen plasma for 15 min. The glasses and AAO film were placed in a desiccator with 200 µl FOTS under vacuum for 1.5 h to achieve a molecular-phobic surface. The glasses and AAO film were soaked in a solution of

3 Mm PEG 6/9 in toluene for 15 h to produce a molecular-philic surface. The samples were then

washed with pure toluene and ethanol to remove resi- duals. Finally, all the modified glasses and AAO films were annealed at 120°C for 1 h. To observe the macro- scopic effect of the NTB orientation after surface treat- ment, CB7CB (1′′, 7′′-bis(4-cyanobiphenyl-4′-yl) heptane), a typical NTB LC material, was filled between two chemically modified glasses via capillary force. The cell gap of the sandwich cells was controlled using

3-µm glass beads. In addition, the CB7CB was loaded into the AAO nanochannels at an isotropic tempera- ture (125°C) via capillary force. The samples were then cooled to an NTB temperature (90°C) at a rate of

1°C min−1. The residual LC material was removed by

scrubbing, and the samples were cooled to room tem- perature at a rate of 5°C min−1.

Characterisation

The temperature of the samples was controlled using a heating stage (LINKAM LTS350, Tadworth, UK) and a fine temperature controller (LINKAM TMS94, Tadworth, UK). The optical anisotropic textures of the NTB LC phases in each sandwich cell were visua- lised using POM (LV100POL, Nikon, Tokyo, Japan) with a cooled charge-coupled device (CCD) colour camera (DS-Ri1, Nikon). The top surface of the AAO was observed using field-emission scanning electron microscopy (FESEM; Hitachi SU5000, Tokyo, Japan). The relative interaction energy between the NTB LC molecule and the SAM-treated glass substrates was estimated by measuring the contact angle (CA) (Phoenix 300 Touch, SEO, Suwon, Korea) at 90°C. The GIXD experiments were performed at the 6D and 9A beamlines in the PLS-II (Pohang Accelerator Laboratory, PAL). The energy of the incident X-ray beam was 11.07 keV, and the sample-to-detector dis- tance (SDD) was 240 mm. All data were recorded over

10 s with a 2D CCD camera (Rayonix SX165, Evanston, USA).

3. Results and discussion

The bent LC molecule – 1´´, 7´´-bis(4-cyanobiphenyl-4

´-yl)heptane (CB7CB) – was synthesised as reported [32,33], by linking two cyanobiphenyl groups with a flexible alkyl spacer (Figure 1(b)). This is a well-known LC molecule whose NTB phase is below the nematic (N) phase upon cooling. To control the structure of the NTB phase, we prepared a porous AAO nanochannel, composed of perpendicularly aligned nanopores made of aluminium oxide, on an aluminium substrate [24,26]. Here, the pores are hexagonally arranged, and each pore has a diameter of 100 nm (DP) and a height

of 5 μm (Figure 1(c)). The CB7CB LC molecules are filled in the porous AAO nanochannels by capillary action, as shown in Figure 1(d).

Along with nanoscale confinement, the inner sur- face of the AAO is chemically modified using two kinds of SAM molecules –FOTS and PEG 6/9 – to control the interaction energy between the surface and the LC molecules (Figure 2(a,b)). The macroscopic chemical affinity between the CB7CB molecules and the SAM-treated substrates was evaluated by measur- ing the CA of an LC droplet. The CA of an LC droplet on the FOTS-treated glass was rather high, ~ 59.5°, which indicates a relatively low surface energy (Figure 2(a)). In contrast, the PEG 6/9-treated cell showed a lower CA, ~ 10.5°, which implies that the CB7CB molecules interact more strongly with the PEG

6/9-treated surface than with the FOTS-treated surface (Figure 2(b)). We prepared 3-μm-thick sandwich cells made of two kinds of SAM-treated glass to compare the macroscopic domain orientation of the LC mole- cules with different interaction energies. In addition, their optical texture was observed using polarised opti- cal microscopy (POM). The images were acquired at

110°C and at 95°C at a cooling rate of 1°C/min, which showed the N and NTB phases, respectively (Figure 2 (c–f)). In both samples, treated with FOTS or PEG 6/9, typical schlieren

textures appeared in the N phase (Figure 2(c,d)), and the conventional polygonal, focal conic domains (FCDs) and rope-like structures appeared in the NTB phase (Figure 2(e,f)). Although both samples appeared to have similar optical texture, the FOTS-treated cell showed smaller domains. This result indicates that many domain boundaries were generated from the greater number of nucleation sites, as expected from the texture in the N phase. Specifically, in the FOTS-treated cell, the macroscopic orientation of the LC domains was very different from typical rod-shaped molecules [26]. When CB7CB molecules were placed on the FOTS-treated substrates, the vertical molecular alignment normally induced in conventional LCs did not occur. Notably, the FOTS- and PEG 6/9-treated samples showed very different affinities, as determined by measuring CA.

To greatly strengthen the surface anchoring on the LC phases, we prepared a CB7CB-infiltrated AAO film for each surface condition. The nanostructures of the N and NTB phases of the CB7CB molecules were observed using GIXD with a synchrotron radiation source. X-ray diffraction is a powerful tool for observing molecular ordering and orientation, using a two-dimensional (2D) CCD camera as a detector [24,26]. In particular, GIXD can reveal in-plane and out-of-plane nanostruc- tures. In our case, the molecular and pseudo-layer

Figure 2. (Colour online) Self-assembled monolayers (SAMs) and polarisation optical images of the sandwiched SAM-treated glass cells. The inner surface of the AAO channels are chemically treated with FOTS (a) or PEG 6/9 (b) silane molecules. Measuring the contact angle of the NTB LC droplets at 90°C reveals the interaction between the LC molecules and the SAM-treated surface, which is either molecule-phobic (a) or molecule-philic (b). Although the surface affinity changes with the surface treatment, a typical schlieren texture appears for the N phase at 110°C (c, d) and broken FCD structures form in the NTB phase at 95°C (e, f). Unlike other LC molecules, these molecules do not show vertical orientation of the FOTS surface. The scale bars are 50 μm.

structure orientation in the LC phase can be observed at an appropriate SDD. Figure 3(a) shows the images acquired at an SDD of 240 mm.

GIXD was performed on the NTB phase (70°C) and N phase (140°C) at a heating rate of 5°C/min. The transi- tion temperatures of the CB7CB material from the crys- tal (Cr) to the NTB phase and from the N phase to the isotropic (Iso) phase in nanoconfinement are 84.5°C and

116°C, respectively. These temperatures are quite differ- ent from those in the bulk state, because of the nano- confinement effect [34,35]. Thus, the NTB phase appeared at 70°C, well below the bulk N–NTB transition temperature, because the crystalline phase is completely suppressed in nanoconfinement [34]. In contrast, the N–Iso transition temperature increases owing to the strong surface anchoring induced by the nanoconfine- ment [35]. The wide-angle intensity variation as a func- tion of temperature can support the shift of the transition

temperature (Figure. S1). The abrupt change in peak intensities at high temperature shows that the liquid crystallinity disappears at T > 170°C, meaning it finally undergoes the isotropic–nematic transition.

The resulting 2D GIXD patterns show orthogonally positioned diffuse arcs in the small- and wide-angle

regions, representing the intercalated and intermolecular distances, which agrees well with a reported result [11] (Figure 3(b–e)). In the NTB phase, both the small- and the wide-angle peaks in Figure 3(b,c) are broader than those of the N phase (Figure 3(d,e)). This behaviour comes from the tilted molecular arrangement of the heliconical structure in the NTB phase. The weak intensity of the small angle peaks in the NTB phase represents the N-like arrangement of intercalated structures, rather than the smectic-like ordering (Figure 3(b,c)). A similar behaviour appeared in the alignment of the NTB phase under a strong magnetic field [11]. Thus, the 2D GIXD patterns show that the heliconical structures are aligned along the nanochannel direction (Ch). Interestingly, the wide-angle peaks are broader for the FOTS-treated AAO nanochannel than for the PEG 6/9-treated sample. This result comes from the change in the degree of ordering for the tilted molecular structure.

At 140°C, the peak positions do not change much from the case of the NTB phase, but they are less broad owing to the more uniaxial alignment of the CB7CB molecules in the N phase. The molecular arrangement of typical rod molecules that exhibit the N phase in nanoconfinement tend to change with differing surface affinity. In this

Figure 3. (Colour online) Grazing incidence X-ray diffraction (GIXD) set-up and 2D diffraction patterns of the NTB and N phases based on surface energy. (a) Experimental set-up for the GIXD measurement. The X-ray beam passes through the sample with an incidence angle. χ is the azimuthal from qxy. The 2D GIXD patterns of the CB7CB were obtained from the FOTS-treated AAO, with a DP of 100 nm, in the NTB phase at 70°C (b) and the N phase at 140°C (d). The same procedure is followed for the PEG-treated AAO at the NTB phase (c) and N phase (e).

regard, parallel and perpendicular orientations with Ch appear for the PEG 6/9- and FOTS-treated cases, respec- tively [26]. However, CB7CB molecules are oriented par- allel to Ch even in the FOTS-treated substrate, which is consistent with the POM images of the FOTS-treated cell (Figure 2). This behaviour will be discussed later in this work.

The molecular orientation in the NTB phase can be determined quantitatively from a 1D plot as a function of χ: the azimuthal angle from 0° at the qxy axis to 90° at the qz axis (Figure 3(a)). The representative wide- and small-angle peaks are chosen as q1 and q2 in the

range of 1.41 ± 0.01 Å−1 and 0.52 ± 0.02 Å−1, respec-

tively. In both the FOTS- and PEG 6/9-treated samples, the 1D plots at q1 have the highest

intensity in the horizontal plane ($\chi \sim 0°$ or 180°). This result indicates a parallel molecular arrangement relative to Ch, on average (Figure 4(a,b)), though the peak broadness varies with temperature and surface treatment. In

contrast, the maximum peaks appear at 90° for q2, which suggests an intercalated structure along Ch (Figure 4(c,d)). To quantitatively evaluate the peak broadness, we calculated the half-width at half-maxi- mum (HWHM) of each plot using Gaussian fit curves [26]. For the FOTS-treated sample, the HWHM at q1 in the N and NTB phases are 48.9° and 53.8°, respec- tively (dashed blue line in Figure 4(a,b) and Figure. S2a, b). The HWHMs at q1 in the N and NTB phases for the PEG 6/9-treated sample are 46.4° and 48.6°, respectively (dashed red line in Figure 4(a,b), and Figure. S2c, d). These results agree well with the expected trend of peak broadness from the 2D GIXD patterns.

The broadened peak in the NTB phase denotes the formation of the heliconical structure. In addition, the tilt and degree of molecular ordering vary with differ- ing surface affinity between the LC molecules and the inner surface of the porous AAO film, while the

Figure 4. (Colour online) A 1D circular cut plotted as a function of χ for the (a, c) NTB phases and (b, d) N phases in the FOTS-treated (blue line) and PEG 6/9- treated (red line) AAO. For reliability, these azimuthal graphs were extracted in the wide-angle region at q1 = 1.42 ± 0.01 Å−1 (a, b) and in the small-angle region at q2 = 0.52 ± 0.02 Å−1 (c, d) where the maximum intensity appears. The light blue and pink dotted lines indicate the half-width at half-maximum (HWHM) of the FOTS-treated and PEG 6/9-treated AAO.

average molecular orientation along Ch remains the same in both SAM-treated samples. In addition, the HWHMs at q2 for the FOTS-treated sample are mea- sured at 53.0° in the N phase and at 54.4° in the NTB phase, while the values for the N phase and the NTB phase are 51.5° and 52.1°, respectively, for the PEG 6/9- treated sample (Figure. S3). The observed relationship of the measured values is consistent with the trend at q1. At the N-to-NTB phase transition (Figure S3a, c goes to Figure S3b, d), the broadness increases slightly, though it changes less in the PEG-treated sample than in the FOTS-treated sample.

Specifically, the HWHM changes by a different amount for q1 and q2. During the transition from the N to the NTB phase, the change in the HWHM at q1 is

$\sim 5.0°$ for the FOTS-treated sample and is $\sim 2.3°$ for the

PEG 6/9-treated sample. In contrast, the change at q2 is

~ 1.3° and ~ 0.7°, respectively (Figure. S2, S3). In addition, the deviation in the HWHMs for the FOTS- and PEG- 6/9-treated samples is larger at q1 than at q2:

~ Δ5° at q1 and ~ Δ 2° at q2 (the difference between

Figure. S2b, d and Figure. S3b, d).

The broadness variation of each peak is related to changes in the tilted state and the order of the LC

molecules. As previously indicated, the HWHM changes at q1 and q2 during the phase transition can be discussed in two parts. First, the change is larger at q1 because this can represent the tilting of molecules to form a heliconical structure, while the small change at q2 occurs because of a change in the intercalated state of the molecular arrangement. Second, the changes in the HWHMs depend on the surface treatment. This behaviour may indicate that the tilting angle of mole- cules during the phase transition is relatively large in the FOTS-treated sample, which means that bent-core molecules need to be arranged with a larger conical angle (Θ) during the formation of the heliconical struc- ture, compared with those in the PEG 6/9-treated sam- ple. The intensity peaks of the PEG 6/9-treated samples (solid red lines in Figure 4) are sharper than those of the FOTS-treated sample (solid blue lines in Figure 4), showing that the CB7CB molecules are better oriented along Ch. In addition, the peak broadness of the PEG

6/9-treated sample does not change much during the phase transition from NTB to N. This behaviour means that the average tilt angle of the molecules must be smaller than that in the FOTS-treated sample, to main- tain the molecular orientation.

Figure 5. (Colour online) Quantitative analysis from the 2D patterns. The 1D line-cut is plotted for the NTB phase in the wide-angle region at χ = 10° (a) and in the small-angle region at χ = 90° (b).

We performed quantitative analysis using a 1D line- cut at χ = 10° and 90° (Figure 5) to understand the structural behaviour in the NTB and N phases with different surface treatments. As reported for the NTB bulk structure of CB7CB, there are two main peaks; one indicates the intermolecular distance at q1 and the other reveals the intercalated spacing that corresponds to the half of molecular length at q2 [11,12]. To gain detailed structural information, the 1D line cut graphs are drawn horizontally (at χ = 10°) at q1 (Figure 5(a)) and vertically (at χ = 90°) at q2 (Figure 5(b)). The

measured molecular distances are q1-FOTS = 1.417 Å−1

(d ~ 4.432 Å) and q1-PEG 6/9 = 1.432 Å−1 (d ~ 4.385 Å)

for the FOTS- and PEG 6/9-treated samples, respec-

tively (Figure 5(a)). The intercalated distance can be estimated as q2-FOTS = 0.499 Å−1 (d ~ 12.585 Å) and q2- PEG 6/9 = 0.540 Å−1 (d ~ 11.630 Å) (Figure 5(b)).

Although these values are similar, the FOTS-treated sample has slightly larger d-spacings than the PEG 6/9- treated sample. These differences remain throughout the whole temperature range (Figure. S4). The FOTS- and PEG 6/9-treated samples show an average intermolecular distance of d1-FOTS = 4.51 Å and d1-PEG 6/9 = 4.41 Å, respectively, and an intercalated distance of d2- FOTS = 12.50 Å and d2-PEG 6/9 = 11.74 Å, respectively (Figure. S4). The intermolecular (Figure. S4a) and inter- calated values (Figure. S4b) are larger in the FOTS-treated sample than in the PEG 6/9-treated sample over the whole temperature range, which indicates that the CB7CB molecules have a relatively loosely packed heli- conical structure. Thus, a more closely packed heliconical structure forms in the PEG-treated AAO nanochannel.

To compare the interaction of the CB7CB molecules based on confinement and surface affinity, we con- ducted the same experiment in the 200-nm-AAO nanochannels, which provided weaker surface anchor- ing and confinement than the 100-nm nanochannels. In the FOTS-treated 200 nm-nanochannel sample, the

sequential 2D GIXD patterns obtained after heating reveal sharp crystal peaks at low temperature and iso- tropic patterns with low intensity at high temperatures (Figure 6(a)). In contrast, the PEG 6/9-treated sample showed a suppressed crystal phase, and the typical crystal peaks at low temperature did not appear. In addition, the change at q1 clearly appears when the N phase transitions to the NTB phase, which is similar to the behaviour of the 100-nm AAO film (Figures 6(b) and 3). However, the NTB phase (at 70°C) at q1 showed broader peaks than the PEG-treated 100-nm-AAO sample (Figures 6(b) and 3(c, e)). This result means that the heliconical structure is not well controlled, though the average helix (H) is aligned along the AAO nanochannel. As shown in the CA results (Figure 2(a,b)), the FOTS-treated surface has lower surface energy than the PEG 6/9-treated surface. Thus, the FOTS-treated surface weakly confines the LC molecules, although this is not observed in the

100-nm-nanochannels. As a result, in the 200-nm FOTS-treated AAO nanochannels, the confinement does not sufficiently control the CB7CB molecules, allowing the LC molecules to behave as in the bulk, as shown in the POM images (Figure 2(c–f)). The insufficient confinement also means the LC molecules are evaporated or removed from the nanochannels to the vacuum near the isotropic phase temperature, which is slightly over 160°C. This behaviour is why we performed the GIXD experiment using heating sequences.

Based on the experimental results, we suggest some possible models for the nanoconfined NTB heliconical structures in the chemically modified AAO nanochan- nels (Figure 7). The heliconical structures are more or less aligned parallel to Ch in both the SAM-treated AAO nanochannels with DP ~ 100 nm owing to the confinement [26,29,36]. In this case, the conical angle

Θ varies depending on the affinity between the CB7CB

Figure 6. (Colour online) Sequential 2D GIXD patterns of the samples with different surface energies. AAOs with a pore diameter of

200 nm were used in both cases.

Figure 7. (Colour online) Models of the heliconical structure in nanoconfinement at different surface energies. (a) A freely packed heliconical structure with a relatively large conical angle (Θ) and intercalated distance, in the FOTS-treated AAO. (b) The tightly packed NTB orientation shows a smaller Θ in the PEG 6/9-treated AAO. Θ is the conical angle.

molecules and the inner surface of the nanochannels. The relatively loosely packed heliconical structure in the FOTS-treated sample has a larger ΘFOTS, which results from the weak interaction between the CB7CB molecule and the FOTS-SAM, which also induces a longer intercalated pitch (Figure 7(a)). In contrast, the PEG 6/9-treated surface has a higher surface energy than the FOTS-treated surface, which leads the mole- cules to form a more tightly packed structure on the inner surface of the nanochannels, so the heliconical structure has a lower tilt angle (ΘPEG 6/9) (Figure 7(b)). In terms of the intrinsic characteristics of the CB7CB molecule in our experiments, it has aromatic and cyano groups on both sides, with a bent-core angle where these two groups have high polarity and thus a large

interaction with the inner surface of the AAO nano- channels. It is, thus, almost impossible to induce the CB7CB molecules to form a perfectly vertical orienta- tion on the surfaces, as shown in the POM images (Figure 2(c, e)). Thus, the NTB structure composed of CB7CB molecules cannot exhibit perfect vertical and horizontal orientations relative to Ch in the FOTS- and PEG-treated AAO nanochannels. However, at least the overall helix (H) can be oriented in one direction.

4. Conclusion

We attempted to control the orientation of the helico- nical structure of the NTB phase in nanoconfinement

using AAO nanochannels. We were able to modulate the packing behaviour of the NTB phase by using dif- ferent SAMs. When using the FOTS SAM, which had lower surface energy, the NTB tended to self-assemble into a more loosely packed structure with more space. In contrast, the PEG 6/9 SAM, with higher surface energy, showed a more tightly packed structure. Our nanoconfinement platform is has higher structural sta- bility than approaches based on external fields such as electric or magnetic fields. Diamagnetic and dielectric anisotropy decrease rapidly upon cooling in the NTB phase [37], so it is difficult to keep a fixed orientation under these fields.

Moreover, spontaneous splay defor- mation occurs at the macroscale, which makes it diffi- cult to maintain the alignment in one direction [10]. Thus, nanoconfinement is a more suitable strategy for controlling the NTB structure. This study improves our collective understanding of the formation mechanism of the NTB structure, and may assist in realising the potential applications of the NTB phase.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Nanoconfined heliconical structure of twist-bend nematic liquid crystal phase

Supplementary information

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Figure S1. Azimuthal angle-varied intensities as a function of temperature at the wide-angle region at q2 = 0.52± 0.02Å-1 for the (a) FOTS- and (b) PEG-treated samples. The AAO pore is fixed at 100nm.

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Figure S2. Gaussian fit curves of the wide-angle intensities at q1 = 1.42± 0.01Å-1 for the (a) FOTS- and (c) PEG-treated case at the N phase and for the (b) FOTS- and (d) PEG-treated case at the NTB phase

Figure S3. Gaussian fit curves of the wide-angle intensities at q2 = 0.52± 0.02Å-1 for the (a) FOTS- and (c) PEG-treated case at the N phase and for the (b) FOTS- and (d) PEG-treated case at the NTB phase

Figure S4. Calculated d values based on the 1D line-cut analysis with varying temperatures. The intermolecular and the intercalated distances are calculated in the wide-angle region at χ

= 10° (a) and in the small-angle region at χ = 90° (b), respectively. The blue and red dots indicate d values of the FOTS-treated and PEG 6/9-treated samples, respectively. The coloured regions represent the normal distribution of d values.