Soft Matter

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/softmatter

Chiral conglomerate observed for a binary mixture between a nematic liquid crystal trimer and 6OCB

Atsushi Yoshizawa,*[a] Yusuke Kato,[a] Haruna Sasaki,[a] Yoichi Takanishi,[b] and Jun Yamamoto[b]

[a] *Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan*
E-mail: ayoshiza@hirosaki-u.ac.jp
[b] *Department of Physics, Graduate School of Science, Kyoto University, Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto, 606-8562, Japan*

Abstract

Dark conglomerates of domains with opposite handedness, which are designated as dark conglomerate phases (DC phases), have attracted much attention. After designing an achiral liquid crystal trimer, 4,4'-bis{7-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]heptyloxy}biphenyl (**1**), which exhibits only a nematic phase, we prepared the binary mixture with some typical rod-like nematic liquid crystals, *i.e.*, 4'-hexyloxy-4-cyanobiphenyl (**6OCB**), 2-(4-hexyloxyphenyl)-5-pentyloxypyrimidine (**PPY**), or 4-methyloxyphenyl 4-hexyloxycyclohexanecarboxylate (**PCA**), and investigated their phase transition behaviour. The binary mixtures containing 55–90 mol% of **6OCB** were found to exhibit a nematic phase and a DC phase of chiral domains with opposite handedness. However, neither **PPY** nor **PCA** induced such a chiral conglomerate phase in the mixture with trimer **1**. We discuss how core–core interactions contribute to produce such a chiral conglomerate phase.

Soft Matter Accepted Manuscript

Introduction

Spontaneous chiral symmetry breaking in soft matter is a well developed field of study. Niori *et al.*[1] discovered polar switching and then Sekine *et al.*[2] suggested chirality in a fluid smectic B2 phase of achiral bent-core molecule **P-n-O-PIMB**. These findings opened new avenues for the study of polar order and chiral superstructures of liquid crystals.[3,4] Chirality-dependent properties in the B2 phase were well explained by Link *et al*. in terms of layer chirality.[5] Some achiral bent-core liquid crystals are known to exhibit optically isotropic phases composed of a conglomerate of domains with opposite handedness, which are designated as dark conglomerate phases (DC phases). Depending on the local structure of these DC phases, they are classifiable as liquid-crystalline sponge phases,[6-13] formed by strongly deformed fluid layers, or as helical nanofilament phases (HNF phases, also assigned as B4 phases).[3,14-18] The sponge phases, usually formed during cooling of the isotropic liquid, have little or no birefringence. The texture under crossed polarizers is nearly dark. Such phases are macroscopically isotropic sponge-like soft solids. The application of high voltage transforms some of such phases to B2 phase.[13,19] The B4 phase is apparently a solid phase, with in-plane hexatic positional ordering in the layers[17] and short-range layer order.[17] The blue phases often exhibit a transparent blue colour. Although no electro-optical switching can be found in the B4 phase, it is SHG active,[4] indicating the existence of polar order in the phase. Results of earlier studies have demonstrated that the smectic layers in both the sponge phases and B4 phases of bent-core liquid crystals tend to have saddle splay curvature.[13,17] The optical activity in the DC phases has been investigated extensively, revealing that it is attributable to the layer chirality[6] or the coupling of molecular conformational chirality to the layer chirality.[18] Aside from the sponge phases and B4 phases, new types of DC phases including modifications of the B4 phase have been observed.[20–24] Helical structures arise not only in the layered phases but also in some nematic phases.[25–37] Chiral domains with opposite handedness have been observed in the nematic phase of some achiral bent-core mesogens.[25–27] The twist-bend nematic phase (N_{tb}) showing domains of opposite handedness was observed for members of achiral α,ω-bis-4-(4’-cyanobiphenyl)alkanes with flexible odd-numbered methylene spacers.[28] The molecules form a helix. The director is tilted with respect to the helical axis in the N_{tb} phase.[29,30] Dozov proposed that inducing some twist can produce a spontaneous bend. Furthermore, he predicted that the N_{tb} phase can exist for bent-shaped molecules.[31] Actually the N_{tb} phase has been observed for liquid crystal dimers with an odd-numbered methylene spacer[32–34] and a bent-core liquid crystal.[35,36]

Soft Matter Accepted Manuscript

Most recently, N_{tb} phase driven by hydrogen bonding has been observed for 4-[6-(4'-cyanobiphenyl-4-yl)pentyloxy]benzoic acid.[37] That evidence reinforces the notion that shape is a key factor stabilizing the N_{tb} phase. Furthermore, symmetry breaking has been reported to occur in nonpolar SmC phases of a 4-cyanoresorcinol bent-core[38] and in liquid phases of polycatenar molecules.[39] Chiral symmetry breaking in mesophases has been observed for bent-shaped molecules, *i.e.*, bent-core LCs and dimers with an odd-numbered spacer.[40–42] A primary factor in the spontaneous symmetry breaking in mesophases is the inherent gross molecular shape of a compound. Fundamental interest in the unusual phenomena of the DC phases persists. Materials exhibiting the DC phase can support important applications, such as organic semiconductors and organic photovoltaics.[43] Actually, material design for the DC phase is an attractive issue.

Recently, we found an equimolecular mixture of achiral liquid crystal trimers exhibiting the HNF phase, suggesting that dipole–dipole interactions between adjacent cores plays an important role in the appearance of HNF phase.[44] This report describes that binary mixtures of an achiral nematic liquid crystal trimer and 4'-hexyloxy-4-cyanobiphenyl (**6OCB**) exhibit a DC phase. This report also presents discussion of how core–core interactions produce such a chiral conglomerate.

Experimental

Materials

Spectroscopic analysis. Purity of the final compound was confirmed using elemental analysis (EA 1110; CE Instruments Ltd.). Infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories Inc.) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JNM-ECA500; JEOL) elucidated the structure of the final product.

Preparation of materials. For use in this study, 5-hydroxy-2-(4-octyloxyphenyl)pyrimidine was purchased from Midori Kagaku Co. Ltd. 1,3-Phenylene bis[4-(4-octyloxyphenyliminomethyl)benzoate] (**P-8-O-PIMB**) was prepared in our laboratory.

4,4'-Bis{7-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]heptyloxy}biphenyl (1). Potassium carbonate (1.82 g, 13.2 mmol) was added to a solution of 4,4'-biphenol (1.12 g, 1.0 mmol) and 1,7-dibromoheptane (4.51 g, 3.0 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 110 °C for 6 h. After filtration of the precipitate,

Soft Matter Accepted Manuscript

water was added to the filtrate. The solution was extracted using chloroform. The combined organic layers were dried on magnesium sulphate. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was purified using column chromatography on silica gel with a toluene : hexane (2:1) mixture as the eluent. The obtained solid was recrystallized from hexane to give 4,4'-(7-bromheptyloxy)biphenyl. Yield: 1.09 g (33.6%).

Potassium carbonate (280 mg, 2.2 mmol) was added to a solution of 4,4'-(7-bromheptyloxy)biphenyl (532 mg, 1.0 mmol) and 4-(5-octyloxypyrimidin-2-yl)phenol (601 mg, 2.0 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 130 °C for 7 h. After filtration of the precipitate, water was added to the filtrate. The solution was extracted using chloroform. The combined organic layers were dried on magnesium sulfate. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was recrystallized from toluene to give the desired compound. Yield: 204 mg (20.9%).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ = 8.40(s, 4H, Ar-**H**), 8.27–8.24 (d, 4H, Ar-**H**, J = 8.7 Hz), 7.46–7.43 (d, 4H, Ar-**H**, J = 8.7 Hz), 6.97–6.92 (d, 8H, Ar-**H**, J = 8.7 Hz), 4.08–3.97 (m, 12H, -OC**H**$_2$-), 1.83–1.79 (m, 12H, aliphatic-**H)**, 1.55–1.29 (m, 32H, aliphatic-**H**), 0.90–0.88 (t, 6H, -C**H**$_3$-, J = 6.9 Hz). IR (KBr):ν cm^{-1}: 2937, 2866 (C-Hstr), 1607 (Ar-H str),1248 (C-O str). Elemental analysis: found: C% 76.04; H% 8.44, N% 5.72 calc. for $C_{62}H_{82}O_6N_4$: C% 76.34; H% 8.31. N% 5.69.

Liquid-crystalline and physical properties

The initial phase assignments and corresponding transition temperatures for each final compound were determined using a polarizing optical microscope (POM, BX-51; Olympus Optical Co. Ltd.) equipped with a temperature control unit (LK-600PM; Japan High Tech). The temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC, DSC 6200; Seiko Instruments Inc.). The X-ray diffraction patterns of the homeotropically aligned sample during cooling were obtained using a real-time X-ray diffractometer (MicroMax–007HF; Rigaku Corp.) equipped with a hot stage and a temperature-control processor. A sample was put on a convex lens, which was then placed in a custom-made temperature-stabilized holder (stability within ±0.1 °C). The phase transition of the sample under the X-ray beam was monitored by observing the texture simultaneously using polarized light microscopy with a CCD camera. The X-ray apparatus was equipped with a platform arrangement and a two-dimensional detector (Image intensifier and CCD C9299–01; Hamamatsu

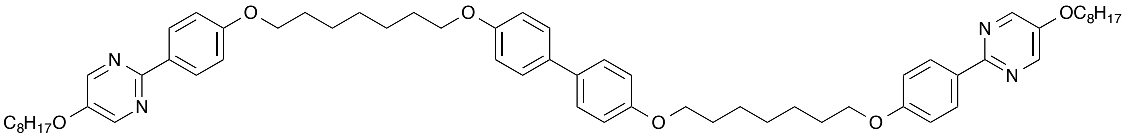
Soft Matter Accepted Manuscript

Photonics KK) for small-angle X-ray scattering (SAXS), and an imaging plate (BAS–SR 127; Fujifilm Corp.) for wide-angle X-ray scattering (WAXS). Then X-rays were generated at 40 kV and 20 mA; the sample was irradiated with a Cu-Kα X-ray beam with confocal mirrors to correlate the incident X-ray beam and increase its intensity. Camera distances from samples to the detectors were ca. 730 mm for SAXS and 40 mm for WAXS.

Electro-optical properties were measured using standard electro-optical techniques. The ITO-coated glass sandwich cells purchased from EHC Corp. were constructed with 2 μm spacers. The unidirectionally buffed inner surfaces had been coated with a polyimide aligning agent.

Results and discussion

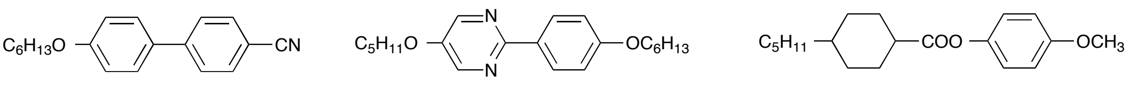
The molecular structure and the phase transition temperatures of trimer **1** determined using POM and DSC are presented in Fig. 1. The compound exhibited only a nematic phase.



1: Cry 145.7 (61.5) N 151.3 (3.9) Iso

Fig. 1 Molecular structure, transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) of transition for trimer **1**.

Compound **1** was mixed with a typical rod-like nematic liquid crystal. Molecular structures and phase transition temperatures of nematic liquid crystals under investigation are presented in Fig.2.



6OCB: Cry 57.0 N 75.5 Iso **PPY**: Cry 70.1 N 89.8 Iso **PCA**: Cry 39.6 N 70.1 Iso

Fig. 2 Molecular structures and transition temperatures (°C) of rod-like nematic liquid crystals under investigation.

We investigated the phase transition behaviour of binary mixtures existing between

Soft Matter Accepted Manuscript

trimer **1** and each rod-like nematic liquid crystal. Figure 3 portrays a phase diagram on cooling between trimer **1** and 4'-hexyloxy-4-cyanobiphenyl (**6OCB**). A dark conglomerate phase (DC) was found to be induced for binary mixtures containing 55–90 mol% of **6OCB**. However, neither 2-(4-hexyloxyphenyl)-5-pentyloxypyrimidine (**PPY**) nor 4-methyloxyphenyl 4-hexyloxycyclohexanecarboxylate (**PCA**) induced such a DC phase in the mixture with trimer **1**. Phase diagrams of trimer **1** and **PPY** or **PCA** are shown respectively in Fig. S1 and Fig. S2 (Electronic Supporting Information). The N phase of trimer **1** was not miscible with that of **PPY** nor that of **PBA**. The mixture with 75 mol% of **PPY** showed a phase transition of Iso 122.8 °C Cry on cooling. The mixture with 75 mol% of **PCA** showed a phase transition of Iso 122.3 °C Cry on cooling.

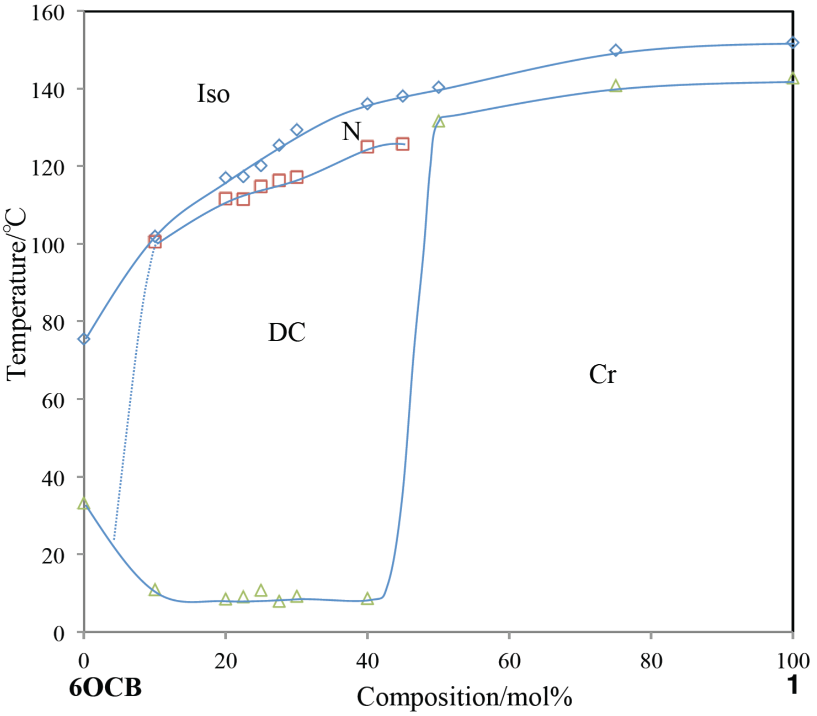


Fig. 3 Phase diagram of trimer **1** and **6OCB**. Blue diamond: Iso–N transition; red square: N–DC transition; green triangle: recrystallization.

Phase transition temperatures and enthalpies of a mixture containing 60 mol% of **6OCB** on cooling were the following: Iso 136.1 °C (1.3 kJ mol^{-1}) N 125.1 °C (12.2 kJ mol^{-1}) DC 8.6 °C (4.9 kJ mol^{-1}) Cry. When heated, the crystal began to melt at 126.8 °C. It changed to an isotropic liquid without the N phase. The melting temperature range was from 126.8–140.3 °C. The cooling DSC thermogram is portrayed in Fig 4.

Soft Matter Accepted Manuscript

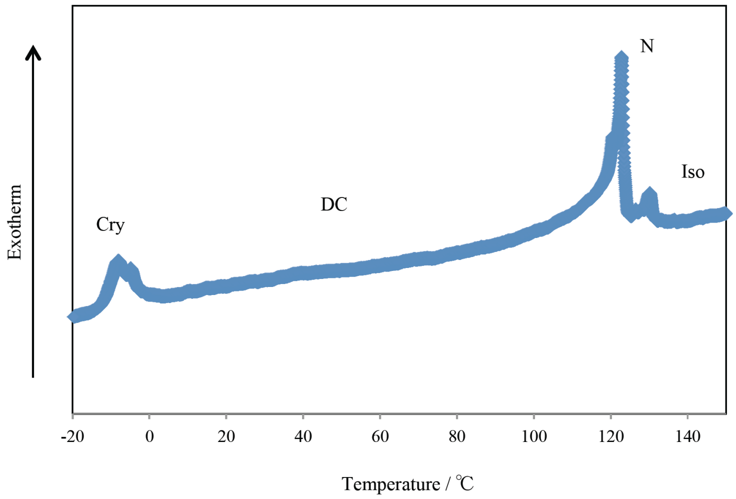


Fig. 4 DSC thermogram of a mixture of trimer **1** (40 mol%) and **6OCB** (60 mol%) on cooling. The cooling rate was 2 °C min^{-1}.

Fig. 5 shows optical textures of a binary mixture of trimer **1** (40 mol%) and **6OCB** (60 mol%) in the DC phase at 114.9 °C under crossed and uncrossed polarizers. The texture of the DC phase under crossed polarizers is nearly dark, suggesting that it is optically isotropic. By observing the sample in the DC phase under slightly uncrossed polarizers (10°), the texture splits into darker and brighter domains. By uncrossing the polarizers in opposite directions by the same angle, the darker and brighter domains exchange. The domain brightness does not change by rotation of the sample between the polarizers. These results indicate that they have optical activity with opposite senses. With respect to the N phase above the DC phase, no chiral nature was detected. Chiral aggregation occurs at the N to DC phase transition.

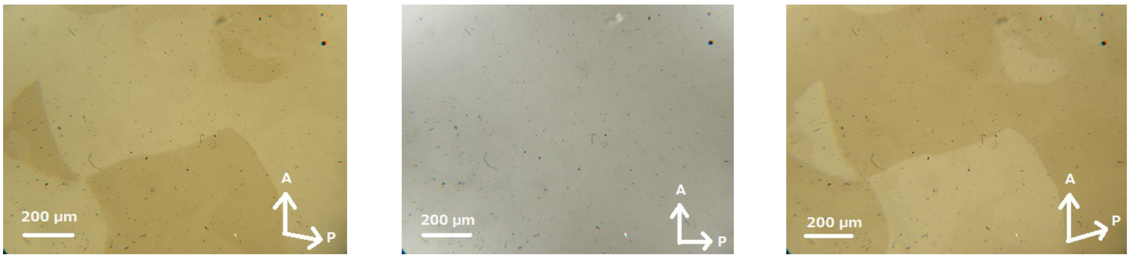


Fig. 5 Polarized optical textures of a binary mixture of trimer **1** (40 mol%) and **6OCB** (60 mol%) on a glass slide with a cover glass in the DC phase at 80 °C with uncrossed and crossed polarizers.

Soft Matter Accepted Manuscript

Soft Matter Accepted Manuscript

Reportedly, mixtures of **P-8-O-PIMB** and 4'-pentyl-4-cyanobiphenyl (**5CB**) exhibit DC phases in a wide range of concentrations of **5CB**.[45] This is explained in terms of chirality transfer from the nanofilaments composed of the bent-shaped molecules to the nematic LCs. The dilution of the HNF phase of **P-8-O-PIMB** by **5CB** without loss of chirality is a direct consequence of the helical nano-filament structure of the DC phases observed for the mixtures. In the binary mixtures of trimer **1** and **6OCB**, the DC phase was observed even in the mixture possessing 90 mol% of **6OCB**, indicating that the DC phase has a HNF structure. However, trimer **1** does not exhibit a HNF phase. Therefore, the appearance of the DC phase does not result from the dilution of the HNF phase as observed for **P-8-O-PIMB**. The driving force for the HNF structure of the mixture differs significantly from that for the classical HNF phase of **P-8-O-PIMB**. Intermolecular interactions between trimer **1** and **6OCB** might produce the HNF phase.

We investigated electro-optical response in the DC phase by application of an AC field to the sample in a homogeneously aligned cell with a gap of 2 μm using a triangle wave with an AC field of ±15 V μm^{-1} at a frequency of 10 Hz. Electro-optical switching was not observed in the DC phase.

To elucidate the phase structure, X-ray measurements were conducted. Alignment was performed by the slow cooling of a small drop of the sample on a convex lens. The N to DC phase transition was confirmed by the texture change. A peak around $2\theta = 1.76°$ was observed in the small angle region in the DC phase at 85.4 °C of a binary mixture of trimer **1** (40 mol%) and **6OCB** (60 mol%), revealing that the DC phase has a layer structure with periodicity length of 49.6 Å. X-ray diffraction pattern and profile in the small angle region in the DC phase are listed in Fig. S3. With respect to the wide-angle region, three peaks $2\theta = 10.8°$, 11.7°, and 14.6° were observed as portrayed in Fig. 6, indicating that it has positional order within the layer as HNF phases for bent-core LCs. This pattern excludes fluid sponge phases, which would show exclusively one completely diffuse wide angle scattering besides the layer reflection.

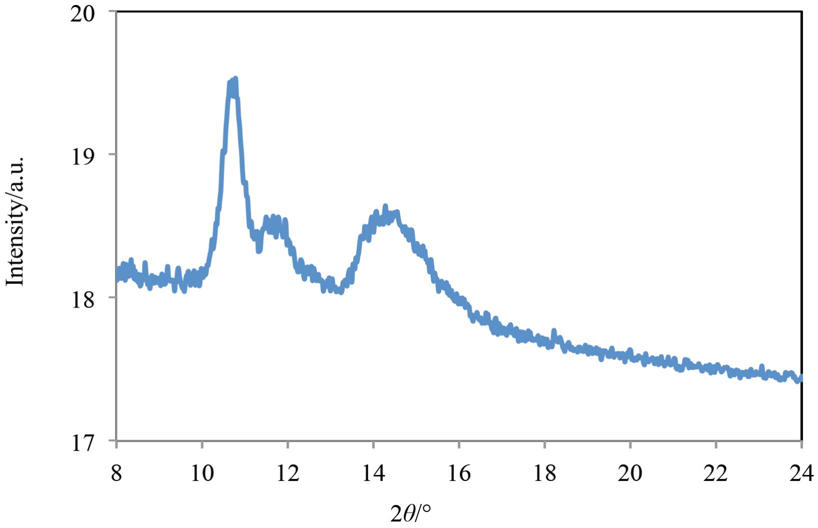


Fig. 6 X-ray diffraction profile in the wide angle region in the DC phase at 85.4 °C of a mixture consisting of trimer **1** (40 mol%) and **6OCB** (60 mol%).

The layer spacing is almost constant as a function of temperature in the DC phase. Figure 7(a) shows that an extended molecular length for trimer **1** with all trans conformation of the spacers is estimated using MOPAC to be 64 Å. The layer spacing is much shorter than the molecular length. The tilt angle based on the XRD measurements is estimated as 40° if the trimer is tilted with the layer normal. This large difference between layer spacing and molecular length is found similarly for the DC phases of the 4-iodo and 4-methylresorcinols derivatives.[23,24] Layer spacing in the previously reported HNF phases is usually close to the molecular length. The shorter layer spacing observed for some resorcinol bent-core LCs are explained in terms of twist conformation of the bent-core molecule.[24] Structure-property relations of the resorcinol bent-core mesogens reveal that conformation chirality attributable to the rigid twist structure plays an important role in the appearance of the DC phase.[24] The molecular length is estimated as 49 Å if trimer **1** has a twisted conformation as portrayed in Fig. 7 (b). The layer spacing in the DC phase of the binary system supports the inference that trimer **1** adopts such a twisted conformation.

Soft Matter Accepted Manuscript

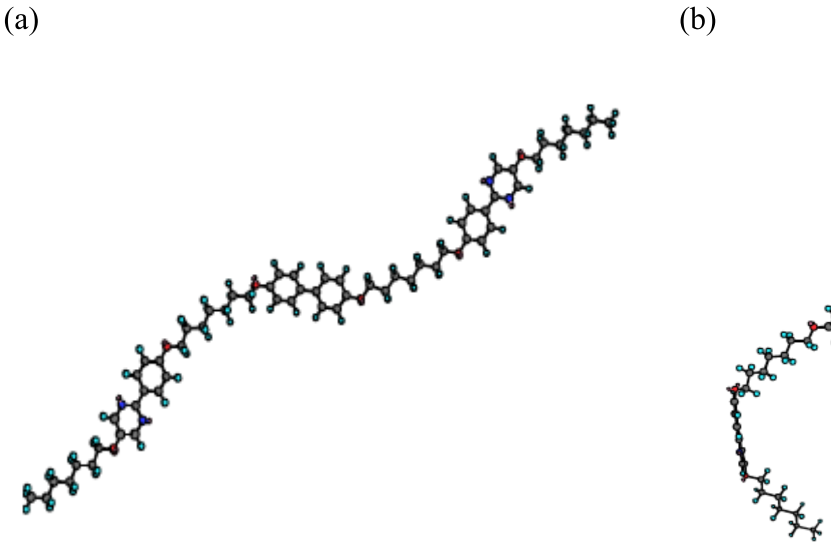


Fig. 7 MOPAC models for trimer **1** with (a) extended conformation and (b) twisted conformation.

To identify the structure, a miscibility study was conducted between the DC phase of the present binary system and the classical HNF phase of a bent-core molecule. We prepared a mixture consisting of trimer **1** (25 mol%) and **6OCB** (75 mol%) for the miscibility study. Figure 8 presents a phase diagram between the DC phase of the binary mixture and B4 (HNF) phase of phenylene bis(octyloxyphenyliminomethyl)benzoate (**P-8-O-PIMB**). The B4 phase of **P-8-O-PIMB** is diluted by the binary mixture up to 50 wt%. However, the DC phase of the binary mixture appears below the B4 phase of **P-8-O-PIMB**. A mixture containing 50 wt% of **P-8-O-PIMB** exhibited the follwoing phase transition: Iso 143.4 °C (11.5 kJ mol^{-1}) B4 111.7 °C (4.9 kJ mol^{-1}) DC –0.5 °C (3.1 kJ mol^{-1}) Cr. Optical textures of the mixture in the B4 and DC phases are listed in Fig. S4. Some dimers with an odd-numbered spacer reportedly exhibit a B4–B4’ phase transition[42]; however, the phase structure of the B4’ phase is not clear.

Soft Matter Accepted Manuscript

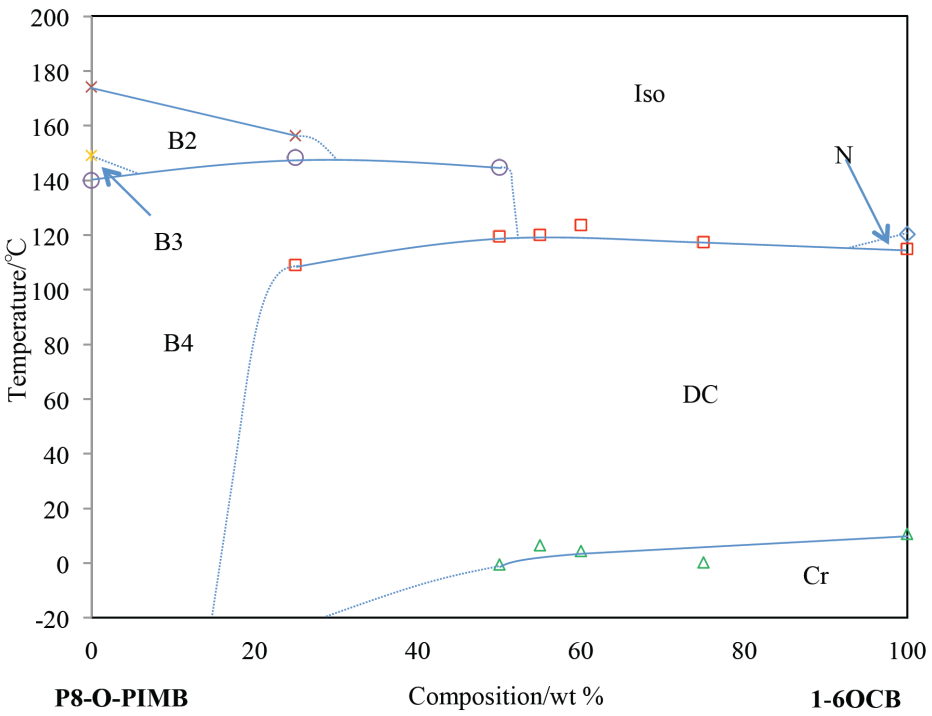


Fig. 8 Phase diagram between **P-8-O-PIMB** and a mixture of compound **1** (25 mol%) and **6OCB** (75 mol%). Purple cross: Iso–B2 transition; yellow cross: B2–B3 transition; purple circle: B3–B4 transition, B2–B4 transition or Iso–B4 transition; green diamond: Iso–N transition; Red squeare: B4–DC transition, Iso–DC transition or N–DC transition; green triangle: recrystallization.

X-ray measurements were conducted on a mixture of **P-8-O-PIMB** (50 wt%) and the trimer **1–6OCB** mixture (50 wt%). Periodicity lengths from SAXS measurements in the B4 and DC phases were, respectively, 48 Å and 46 Å. X-ray diffraction profiles in the small angle region in the those phases are shown in Fig. S5. With respect to the wide angle region, two peaks at $2\theta = 11.8°$ and $14.2°$ were observed in the B4 phase (Fig. 9(a)). Cooling to the DC phase (Fig. 9(b)), a peak at $2\theta = 10.8°$ characteristic to the DC phase appeared in addition to those peaks ($2\theta = 12.1°$ and $14.3°$) observed in the B4. The peak at $2\theta = 10.8°$ suggests that the longer periodicity appears at the B4 to DC transition.

Soft Matter Accepted Manuscript

Soft Matter Accepted Manuscript

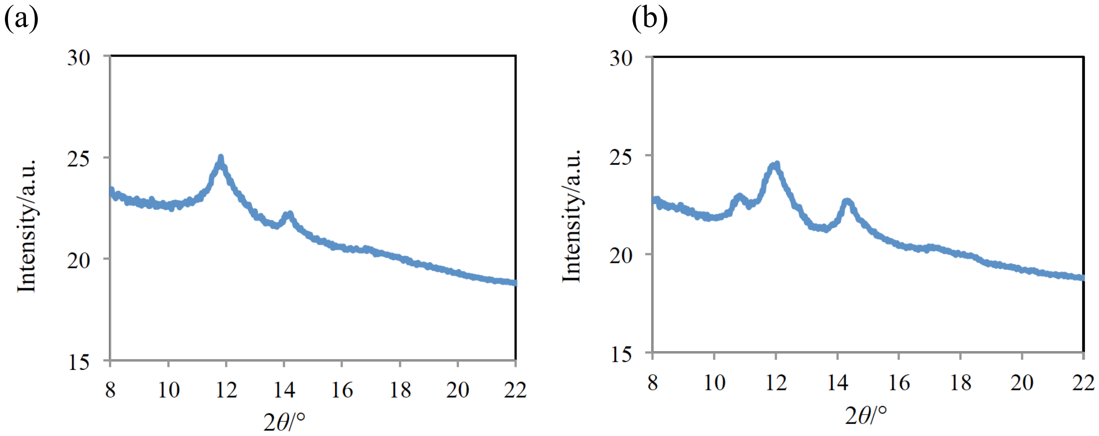


Fig. 9 X-ray diffraction profile in the wide angle region in (a) the B4 phase at 135.4 °C and (b) the DC phase at 85.4 °C of a mixture of **P-8-O-PIMB** (50 wt%) and the trimer **1–6OCB** mixture (50 wt%).

The phase diagram reveals the following. The B4 phase of **P-8-O-PIMB** is probably diluted by **6OCB**. Although the DC phase below the B4 phase also has a helical nanofilament structure, a longer periodicity length observed for a peak at $2\theta = 10.8°$ exists within a layer in the DC phase in comparison to the classical B4 phase. The B4 to DC phase transition can be driven by another factor that is responsible for the peak.

We next discuss how chirality arises in the DC phase of the binary mixture of trimer **1** and **6OCB**. As described above, the DC phase might have a helical nanofilament structure, but the driving force for the DC phase is thought to differ from that for the classical HNF phase. Bent-core molecules exhibiting DC phases tend to form layer structures. Therefore, they do not show a nematic phase. With respect to the present binary system of trimer **1** and **6OCB**, both nematic phases are miscible. The binary mixtures show the conventional nematic phase. The molecular organization has no chiral origin in the N phase. Intermolecular interactions between trimer **1** and **6OCB** produce the chiral nature in the DC phase. It is noteworthy that neither phenylpyrimidine derivative nor phenyl cyclohexanecarboxylate derivative induces such a DC phase in the mixture with trimer **1**. A cyanobiphenyl unit is known to interact with a phenylpyrimidine unit via a specific core–core interaction to induce a smectic A phase.[46] Core–core interaction might play an important role in the appearance of the DC phase. The layer spacing is much shorter than the molecular length of trimer **1**, which was also observed for a new type of DC phases of some 4-substituted resorcinol derived bent-core mesogens possessing azobenzene wings.[23,24] The phase formation is explained as follows.[24] Because azobenzene wings are completely flat, the only source of conformation chirality is the central part of the molecules, *i.e.* the connections between the resorcinol core and azobenzene wings. The substituent produces the twist of between the planes of the azobenzene wings. The difficulty in the parallel packing of the highly twisted molecular species is favourable for chiral segregation and layer distortion. Figure 10 presents a molecular organization model for the origin of chirality for the binary mixture of achiral trimer **1** and **6OCB**. The trimer is thought to combine two bent-shaped dimers. We assume that core–core interactions between cyanobiphenyl and phenylpyrimidine units induce the twist orientation between the pseudodimers within trimer **1**, which can cause twisting of the central biphenyl. This twist conformation chirality is regarded as the origin of the appearance of the DC phase. The twisted trimer **1** might induce the greater periodicity length within each layer in the DC phase. According to a report by Tschierske *et al.*,[24] the twisted trimer packing is in competition with the formation of extended flat layers to lead layer deformation.

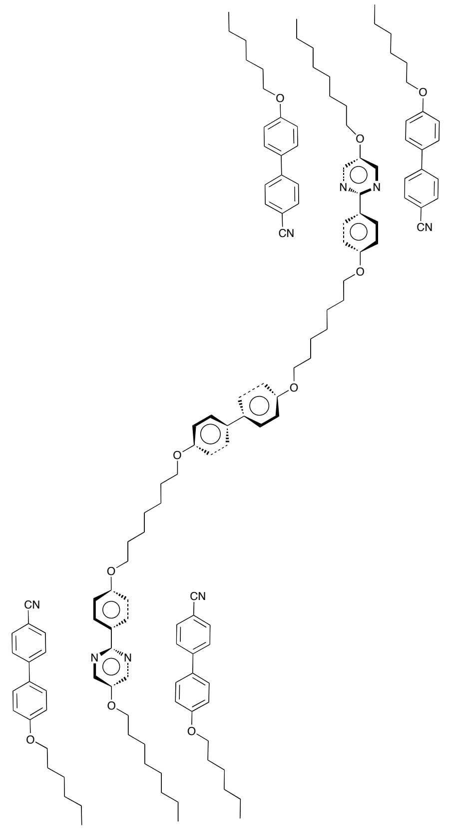


Fig. 10 Molecular organization model for the origin of chirality for the binary mixture of achiral trimer **1** and **6OCB**.

Soft Matter Accepted Manuscript

Conclusions

The dark conglomerate of domains with opposite handedness was induced in binary mixtures of achiral nematic liquid crystal trimer **1** and **6OCB**. The DC phase is thought to have a helical nanofilament structure. It is a low-temperature phase of a classical HNF (B4) phase. Interaction between a phenylpyrimidine unit of trimer **1** and a cyanobiphenyl unit of **6OCB** can produce a twist conformation of the central biphenyl of the trimer, which induces chiral segregation and layer deformation to drive the chiral conglomerate. These findings provide important information indicating how chirality arises in soft matter.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research (no. 25107702) on the Innovation Areas: "Fusion Materials" (Area no 22006) from MEXT.

References

1. T. Niori, T. Sekine, J. Watanabe and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.
2. T. Sekine, T. Niori, M. Sone, J. Watanabe, S. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys*., 1997, **36**, 6455.
3. H. Takezoe and Y. Takanishi, *Jpn. J. Appl. Phys.*, 2006, **45**, 597.
4. A. Eremin and A. Jakli, *Soft Matter*, 2013, **9**, 615.
5. D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblova and D. M. Walba, *Science*, 1997, **278**, 1924.
6. G. Heppke, D. D. Parghi and H. Sawade, *Liq. Cryst.*, 2000, **27**, 313.
7. J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe and J. Watanabe, *J. Am. Chem. Soc.*, 2000, **122**, 7441.
8. H.N. S.Murthy and B. K. Sadashiva, *Liq. Cryst.*, 2000, **29**, 1223.
9. G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl and C. Tschierske, *Angew. Chem., Int. Ed.*, 2002, **41**, 2408.
10. A. Eremin, S. Diele, G. Pelzl and W. Weissflog, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top*., 2003, **67**, 020702.
11. R. A. Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2003, **30**, 1031.
12. J. Etxebarria, C. L. Folcia, J. Ortega and M. B. Ros, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2003, **67**, 042702.
13. L. E. Hough, M. Spannuth, M. Nakata, D. A. Coleman, C. D. Jones, G. Dantlgraber, C. Tschierske, J. Watanabe, E. Körblova, D. M. Walba, J. E. Maclennan, M. A. Glaser and N. A. Clark, *Science*, 2009, **325**, 452.

Soft Matter Accepted Manuscript

14. R. A. Reddy and C. Tschierske, *J. Mater. Chem.*, 2006, **16**, 907.

15. H. Niwano, M. Nakata, J. Thisayukta, D. R. Link, H. Takezoe and J.Watanabe, *J. Phys. Chem. B*, 2004, **108**, 14889.

16. H. Takezoe, *Top. Curr. Chem.*, 2012, **318**, 303.

17. E. Hough, H. T. Jung, D. Kruerke, M. S. Heberling, M. Nakata, C. D. Jones, D. Chen, D. R. Link, J. Zasadzinski, G. Heppke, J. P. Rabe, W. Stocker, E. Korblova, D. M. Walba, M. A. Glaser and N. A. Clark, *Science*, 2009, **325**, 456.

18. J. Thisayukta, H. Takezoe and J. Watanabe, *Jpn. J. Appl. Phys.*, 2001, **40**, 3277.

19. M. Nagaraj, K. Usami, Z. Zhang, V. Görtz, J. W. Goodby and H. F. Gleeson, *Liq. Cryst.*, 2014, **41**, 800.

20. (a) H. Ocak, B. Bilgin-Eran, M. Prehm and C. Tschierske, *Soft Matter*, 2012, **8**, 7773; (b) H. Ocak, B. Bilgin-Eran, M. Prehm and C. Tschierske, *Soft Matter*, 2013, 9, 4590.

21. E. Tsai, J. M. Richardson, E. Körblova, M. Nakata, D. Chen, Y. Shen, R. Shao, N. A. Clark and D. M. Walba, *Ang. Chem. Int. Ed.*, 2013, **52**, 5254.

22. G. B. Deepa, S. Radhika, B. K. Sadashiva and R. Pratibha, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2013, **87**, 062508.

23. M. Alaasar, M. Prehm, M. Brautzsch and C. Tschierske, *J. Mater. Chem. C*, 2014, **2**, 5487.

24. M. Alaasar, M. Prehm, M. Brautzsch and C. Tschierske, *Soft Matter*, 2014, **10**, 7285.

25. G. Pelzl, A. Eremin, S. Diele, H. Kresse and W. Weissflog, *J. Mater. Chem.*, 2002, **12**, 2591.

26. T. Niori, J. Yamamoto and H. Yokoyama, *Mol. Cryst. Liq. Cryst.*, 2004, **409**, 475.

27. (a)V. Görtz and J. W. Goodby, *Chem. Commun.*, 2005, 3262; (b) V. Görtz, C. Southern, N. W. Roberts, H. F. Glleeson and J. W. Goodby, *Soft Matter*, 2009, **5**, 463.

28. M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de La Fuente, D. J. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi, H. Zimmermann, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **84**, 031704.

29. V. Borshch, Y. K. Kim, J. Xiang, M. Gao, A. Jakli, V. P. Panov, J. K. Vij, C. T. Imrie, M. G. Tamba, G. H. Mehl and O. D. Lavrentovich, *Nat. Commun.* 2013, **4**, 2635.

30. D. Chen, J. H. Porada, J. B. Hooper, K. Klittnick, Y. Shen, M. R. Tuchband, E. Körblova, D. Bedrov, D. M. Walba, M. A. Glaser, J. E. Maclennan and N. A. Clark,

Soft Matter Accepted Manuscript

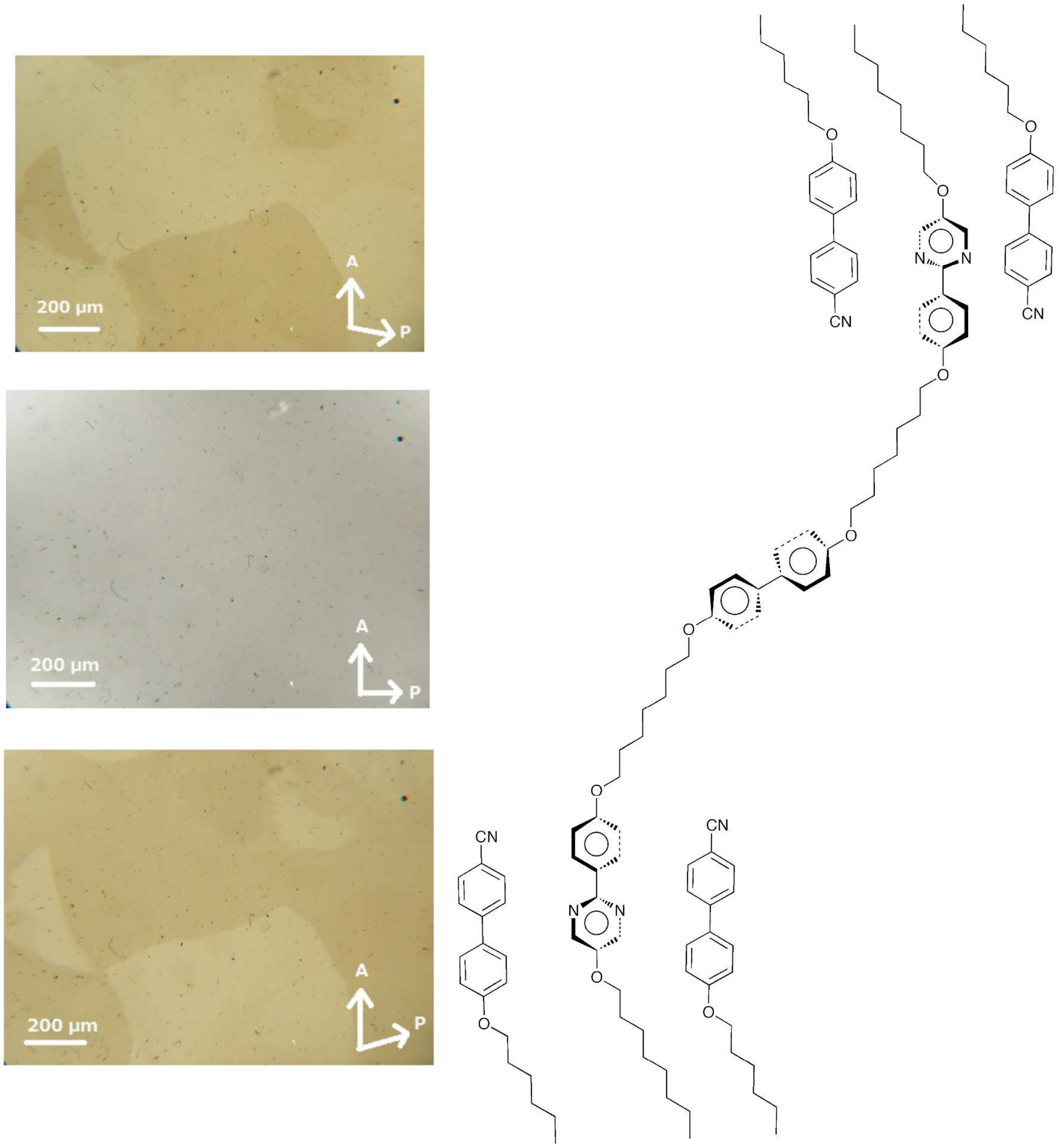
Proc. Natl. Acad. Sci. USA, 2013, **110**, 15931.

31. (a) I. Dozov, *Europhys. Lett.*, 2001, **56**, 247; (b) C. Meyer, G. R. Luckhurst and I. Dozov, *Phys. Rev. Lett.*, 2013, **111**, 067801.
32. V. P. Panov, M. Nagaraj, J. K. Vij, Y. P. Panarin, A. Kohlmeier, M. G. Tamba, R. A. Lewis and G. H. Mehl, *Phys. Rev. Lett.*, 2010, **105**, 167801.
33. P. A. Henderson and C. T. Imrie, *Liq. Cryst.*, 2011, **38**, 1407–1414.
34. R. Mandle, E. J. Davis, C. T. Archbold, S. J. Cowling and J. W. Goodby, *J. Mater. Chem. C*, 2014, **2**, 556.
35. M. W. Schröder, S. Diele, G. Pelzl, U. Dunemann, H. Kresse and W. Weissflog, *J. Mater. Chem.*, 2003, **13**, 1877.
36. D. Chen, M. Nakata, R. Shao, M. R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D. M. Walba,M. A. Glaser, J. E. Maclennan and N. A. Clark, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2014, **89**, 022506.
37. S. M. Jansze, A. Martinez-Felipe, J. M. D. Storey, A. T. M. Marcelis and C. T. Imrie, *Ang. Chem. Int. Ed.*, 2015, **54**, 643.
38. M. Alaasar, M. Prehem, M. Nagaraj, J. K. Vij and C. Tschierske, *Adv. Mater.*, 2013, **25**, 2186.
39. C. Dressel, T. Reppe, M. Prehm, M. Brautzsch and C. Tschierske, *Nat. Chem.*, 2014, **6**, 971.
40. (a) T. Izumi, S. Kang, T. Niori, Y. Takanishi, H. Takezoe and J. Watanabe, *Jpn. J. Appl. Phys.*, 2006, **45**, 1506; (b) T. Ueda, S. Masuko, F. ASraoka, K. Ishikawa and H. Takezoe, *Angew. Chem. Int. Ed.*, 2013, **52**, 6863.
41. (a) E. Bialecka-Florjanczyk, I. Sledzinska, E. Gorecka and J. Przedmojski, *Liq. Cryst.*, 2008, **35**, 401; (b) A. Zep, M. Salamonczyk, N. vaupotic, D. Pociecha and E. Gorecka, *Chem. Comm.*, 2013, **49**, 3119.
42. A. Zep, K. Sitkowska, D. Pociecha and E. Gorecka, *J. Mater. Chem. C*, 2014, **2**, 2323.
43. D. M. Walba, US 8,963,140 B2 (2013).
44. H. Sasaki, Y. Takanishi, J. Yamamoto and A.Yoshizawa, *J. Phys. Chem. B*, 2015, **119**, 4531.
45. T. Otani, F. Araoka, K. Ishikawa and H. Takezoe, *J. Am. Chem. Soc.*, 2009, **131**, 12368.
46. A. Yoshizawa, Y. Soeda and I. Nishiyama, *J. Mater. Chem.*, 1995, **5**, 675.

Soft Matter Accepted Manuscript

Graphical Abstract

Interaction between a phenylpyrimidine unit of trimer **1** and a cyanobiphenyl unit of **6OCB** can produce a twist conformation of the central biphenyl of the trimer, which induces chiral segregation and layer deformation to drive the chiral conglomerate.



Soft Matter Accepted Manuscript