

Stable amorphous blue phase of bent-core nematic liquid crystals doped with a chiral material†

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We report an induction of the blue phase III (BPIII) at a relatively low and wide (over 20 °C) temperature range in nematogenic achiral bent-core liquid crystals doped with a high twisting power chiral material. The pitch decreases with increasing chiral dopant ratio, and easily reaches the ultraviolet wavelength, so that completely dark texture is obtained under crossed polarizers. Electrooptical switching was achieved in a time range of a few to a few tens of milliseconds. We propose for the stabilization of BPIII that broad-temperature range smectic nano-clusters inhibit the long-range order of the double twisted helical structures, and also inhibit possible separation of chiral dopants from the mixture.

Introduction

The polarity and chirality of bent-core (BC) liquid crystals (LCs) is one of the most exciting fields of current liquid crystal research.^{1,2} Studies of the physical properties of bent-core nematic (BCN) materials have recently found extraordinary properties compared to the nematics of rod-like molecules.² The influence of achiral BC LCs on enhancing chirality was first reported by Thisayukta *et al.*³ who described an increase of twisting power in chiral nematic (N*) liquid crystals by the introduction of achiral BC molecules. Nakata *et al.*⁴ found the induction of blue phases (BPs), when ordinary N* LCs were doped with achiral bent-core molecules. BPs are three-dimensional liquid crystal (LC) phases characterized by double twist helical structures, known to exist between the N* and isotropic phases. Three BPs are known: body-centered cubic (BPI), a simple cubic (BP II), and an amorphous (BPIII) phases.⁵ Naturally occurring BPs are restricted in narrow (about 1 K or less) temperature ranges,⁶ but recently larger temperature range BPs have been made by polymer stabilization⁷ and by use of mixtures of dimeric LC molecules with a chiral dopant.⁸ These discoveries made BP materials viable for novel LC displays.⁹ But there are several problems remained unsolved such as processability and reliability.

Recently Yelamagad *et al.*¹⁰ synthesized optically pure LC dimers with strong molecular chirality by covalently linking an achiral bent-core unit with a bulky pro-mesogenic rod-like chiral entity through a flexible spacer, and showed that these materials

could display BPIII over 20 °C range above a N* phase (above 150 °C). This observation is very similar to that found for T-shaped molecules^{11,12} and suggests that the biaxial shape of the molecules is responsible for the stabilization of BPIII though no explanation for underlying physical properties has been suggested yet. These studies motivated us to utilize BCNs doped with strongly chiral molecules to stabilize BPs.

In this paper we will describe the induction of BPIII by simply doping achiral BCNs with a strong chiral dopant and propose a plausible mechanism that can explain the occurrence of the BPIII phase instead of the BPI or BP II phases.

Experimental

For our studies we chose a well studied BCN material CIPbis10BB,¹³ and two relatively new materials S2141 and S110-see Figure S1 in Supplementary Information (SI)-that have similar mesophase ranges. As a control material, the calamitic LC, 4-n-octyloxyphenyl 4'-n-hexyloxybenzoate (6OO8)¹⁴ was used, because it is known to be highly miscible with CIPbis10BB, and the structure of the material is similar to that of the arms of that BCN.¹⁵ The molecular structures of these LCs are shown in Fig. 1. For chiral dopant we chose the same BDH1281 (Merck Chemicals) as that used in ref. 17 for its very high helical twisting power.

The phases of the mixtures, ranging from 0% to 10% chiral dopant by weight, were identified by polarizing optical microscopy (POM; Nikon OPTIPHOT-POL and Olympus BX51), differential scanning calorimetry (DSC; PerkinElmer Pyris Diamond), and electrooptic (EO) techniques. Optical rotation measurements were performed using a Fiber-Lite DC-950 light source and an Ocean Optics HR2000 + ES mini spectrometer in conjunction with Omega temperature controllers. Switching speed was measured using a Chino DB1000 temperature controller and a Wavetek 75 arbitrary waveform generator amplified using an NF Electronic Instruments 4010 amplifier. For temperature control Mettler FP90 and Instec STC200 heat stage controllers were used.

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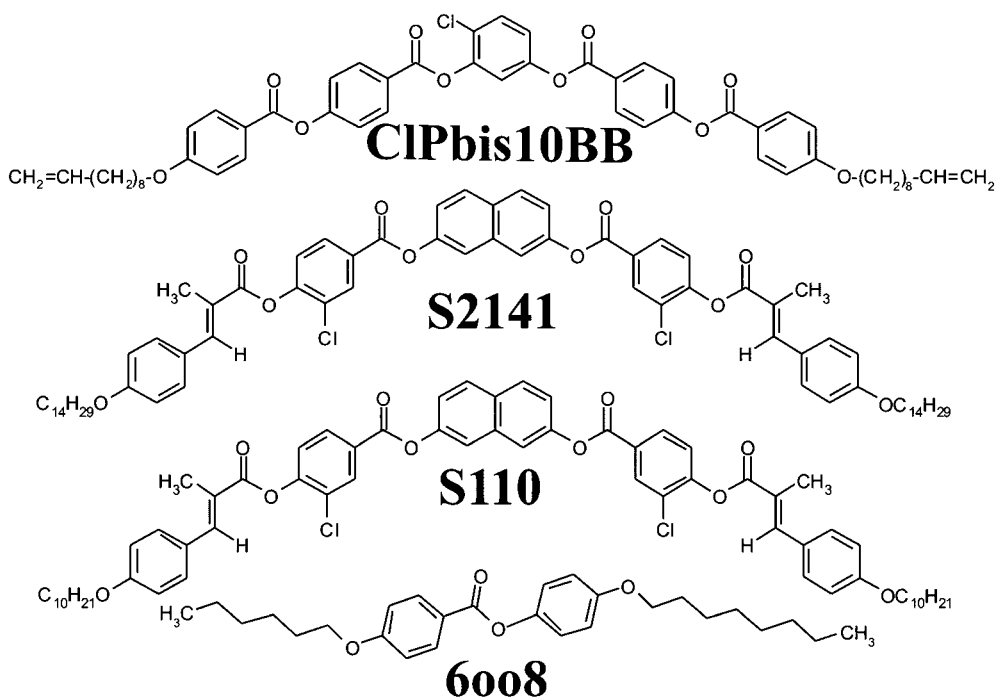


Fig. 1 Molecular structures of the materials studied. From top to down: CIPbis10BB [Cr 83 °C (Cr 52 °C N 75 °C) Iso], S2141 [Cr 94.0 °C (SmCP_A 86.5 °C) N 104.2 °C Iso], and S110 [Cr 97.0 °C (Col, 81.5 °C) N 107.2 °C Iso]; Rod-like nematic 6008 [Cr 38 °C SmC 48 °C N 90 °C Iso]. Sequences with parentheses indicate a monotropic phase, and we used the following abbreviations: Crystal (Cr); Isotropic Fluid (Iso); Columnar with rectangular lattice (Col_r); Nematic (N); Smectic with director tilted with respect to the fluid layers (SmC).

Results and discussion

For all three bent-core materials, when mixed with BDH1281 above 1–2 wt% concentrations, the BPIII phase replaces their original nematic phase. Particularly at chiral dopant concentrations ranging from 3.0–3.2 wt%, the BPIII phases range from 16–25 °C wide. Let us first describe the results of the mixtures of CIPbis10BB and BDH1281. We prepared a contact cell of CIPbis10BB without BDH1281 and with 4.9 wt% BDH1281 and observed under a microscope at 65.5 °C, as shown in Fig. 2(a). We can see Schlieren-like texture on the left hand side and some disordered colored texture in the middle region suggesting the existence of N and N* phases, respectively. The texture becomes uniform from the middle to the right hand side and the reflected light becomes darker. To confirm the N* phase, we also prepared a contact cell of CIPbis10BB without BDH1281 and with 0.5 wt% BDH1281 and observed the texture at 74.5 °C (Fig. 2(b)). A red color on the left bottom is due to flow birefringence in the N phase, so that the brightness changes by cell rotation. Next to the red region, we can clearly observe Grandjean steps, whose colors do not change by rotating the cell, indicating the selective reflection color of N*. For detailed investigation, we prepared four mixtures with 1.4, 3.2, 4.9 and 7.2 wt% BDH1281, and observed the textures at 70.6 °C, 69 °C, 65 °C, and 58.8 °C, respectively. We found that all the mixtures show always uniform textures, as shown in Fig. 2(c).

A phase diagram obtained by textural observation is shown in Fig. 2(d); the BPIII-Iso transition temperature decreased with increasing chiral dopant concentration. By contrast the crystallization temperature is comparatively unaffected by the concentration of chiral dopant. Each mixture shows uniform texture

which darkens from an initial uniform bright blue (1.4 wt%) to complete dark (4.9 and 7.2 wt%), as shown in Fig. 2(c). Over the whole temperature range of the liquid crystal, uniform color was preserved with color shift toward red with decreasing temperature. The DSC results on the pure CIPbis10BB and its mixtures with BDH1281 are shown in Fig. S2 (Supporting information). Due to the reasons mentioned below, we assign this phase as BPIII: (i) The texture is uniform and none of a typical texture of chiral nematic (cholesteric) such as fan-shaped, oily streaks, Grandjean or so is observed in the cell without surface treatment; (ii) Depending on the concentration of chiral dopant, the uniform color changed from bright blue to dark blue, and dark, but none of them show any sharp reflection peak in their reflectivity spectra as was seen in the literature;¹⁶ (iii) The cholesteric phase does exist in the mixture with extremely small amount of dopant, as confirmed using a contact cell (Fig. 2 (b)).

Based on the above observations, we can conclude that the whole mesogenic temperature range (about 23 °C in the mixture of 1.4 wt% chiral content) is occupied by BPIII. This gives the hope that broad-range room-temperature BP materials can be formed by adding small amounts of chiral dopant to achiral bent-core nematics. In contrast to BP materials using calamitic LCs and lower-HTP chiral dopants that may require 30 wt% dopants^{17,18,19} or more, in bent-core nematics the BDH1281-induced blue phase appears at as low as 1–2 wt% concentrations. This simple and effective approach is different from either method described in ref. 10 and 12.

To further explore the relationship between BCNs and BPIII and to support the tendency of stabilizing BPIII in achiral BCN with BDH1281, we also examined the mixture of S110 and 3.1 wt% BDH1281. Fig. 3 shows textures of these mixtures with the

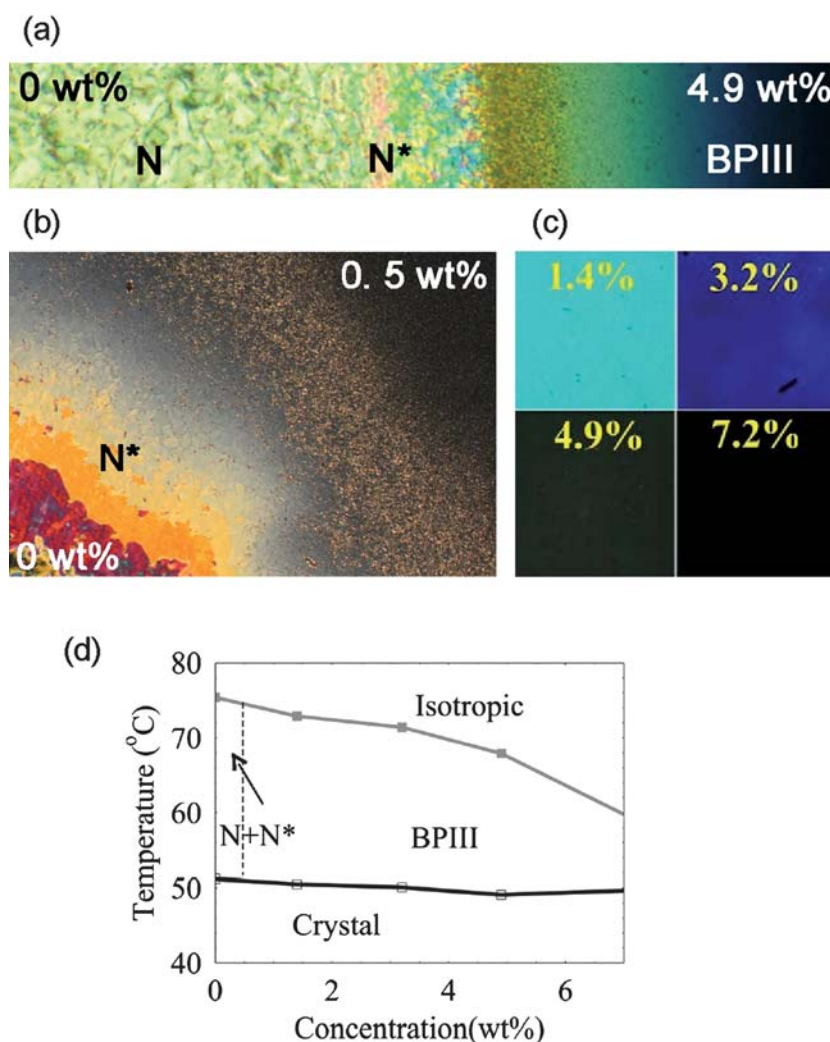


Fig. 2 Illustration of the BPIII phase obtained from CIPbis10BB – BDH1281 mixtures. (a) Texture of a contact cell for CIPbis10BB and BDH1281 representing an approximate concentration gradient between 0 and 4.9 wt% BDH1281 at 65.5 °C. The picture represents 0.63 mm × 0.1 mm area. (b) Texture of a contact cell for CIPbis10BB and BDH1281 representing an approximate concentration gradient between 0 and 0.5 wt% BDH1281 at 74.5 °C. The picture represents 1.16 mm × 0.77 mm area. (c) Typical textures as seen by POM at different chiral dopant concentrations, 1.4, 3.2, 4.9, and 7.2 wt% at 70.6 °C, 69 °C, 65 °C, and 58.8 °C, respectively. All of them show uniform colors suggesting BPIII. The individual pictures represent 160 μm × 160 μm areas. (d) Phase diagram of the CIPbis10BB and BDH1281 mixture system in cooling. Note: such as the pure CIPbis10BB is monotropic, so the observed BPIII phase as well. Dotted line is a boundary estimated by (b).

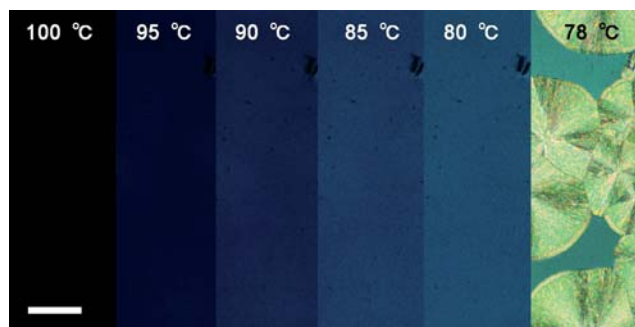


Fig. 3 Polarizing photomicrographs of the mixture of S110 with 3.1 wt% BDH1281 in a 10 μm thick cell. Uniform colored textures suggesting BPIII are observed over 20 °C wide, becoming bluer with decreasing temperature and finally transitioned to Col_r phase. In heating the crystal phase melts to nematic only at 97 °C and the BPIII range is about 10 °C wide. The scale bar is 100 μm long.

phase sequence, Iso 104.5 °C BPIII 79.3 °C Col_r. Uniform textures are observed in a wide temperature range over 20 °C (100–80 °C), as shown in Fig. 3; a uniform dark texture gradually becomes brighter with decreasing temperature and at lower temperature (79.3 °C) columnar rectangular (Col_r) phase emerges. This series of photomicrographs verify the emergence of BPIII over a wide temperature range.

The blue textures are not sensitive to the alignment; they are optically active and isotropic. The temperature dependence of the rotation angle Φ in unit thickness of slab Φ/d was measured using the mixture of CIPbis10BB with 3.2 wt% BDH1281. The result shown in Fig. 4(a) is qualitatively similar to those measured in highly chiral calamitic LCs^{20,21} but with some very important quantitative differences: (i) the BPIII range is much larger; (ii) the optical activity Φ/d is about two orders of magnitude larger in the bent-core BPIII than in chiral calamitic LCs;^{21,22} (iii) the sign of the optical activity is the same in the

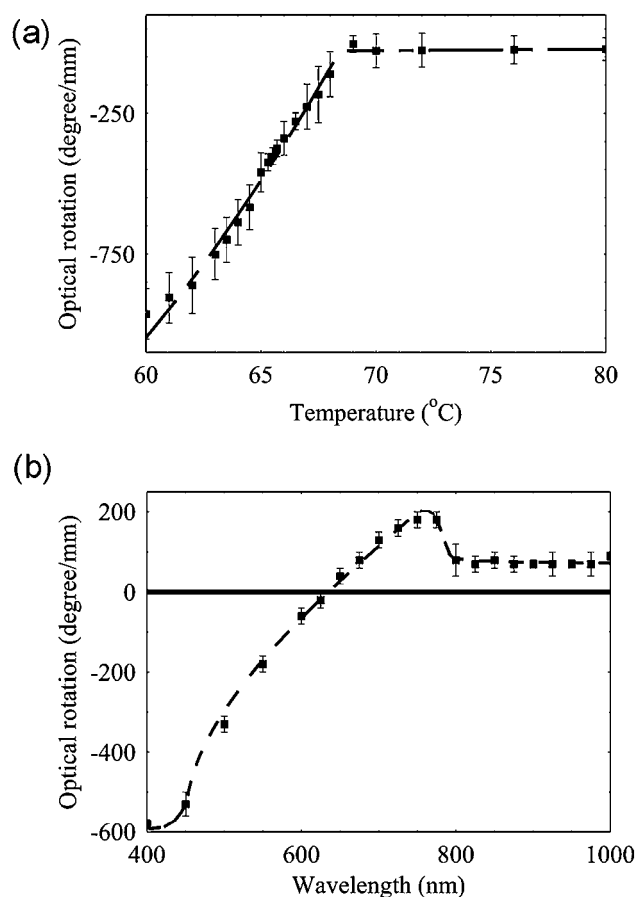


Fig. 4 (a) Optical activity as a function of temperature at 532 nm. (b) Wavelength dependence (dispersion) of optical rotation at $T_{1-BPIII} - T = 3^\circ\text{C}$.

isotropic phase as in the BPIII range (whereas in calamitics it is usually the opposite).²² The dispersion of the optical rotation (ORD) is qualitatively similar to the BPIII phases of highly chiral cholesteryl derivatives in the sense that the optical activities are stronger at shorter wavelengths and there is a sign inversion at longer wavelengths [Fig. 4(b)].²² However, the wavelength of the sign inversion is much larger in BCNs.

BPIII materials can undergo a BPIII-N transition with applied electric fields.¹⁴ To see if this is indeed the case, we conducted electrooptical (EO) experiments in the BPIII phase using a cell with interdigitated in-plane electrodes. The result at 72.8°C of 1.4 wt% BDH1281 in CIPbis10BB under a sinusoidal voltage of $57 V_{p-p}$, 1 kHz is shown in Fig. 5(a). The brightness and color change due to field-induced BPIII-N transition is clearly observed on the right-hand side. In the mixture of the lowest concentration studied (1.4 wt% chiral dopant) the switching was monostable, *i.e.*, it could be switched to the bright N phase, but the switched cell would not return back to a dark state when the field was removed. In these cases, the cells had to be heated to isotropic and re-cooled in order to return to the BPIII phase-indicative of a first order transition between the N and BPIII phases. Importantly, at ≥ 3.2 wt% dopant concentrations the texture could be repeatedly switched in the entire BPIII temperature range. For the switching time, as an example, the rise and decay times in CIPbis10BB with 3.2 wt% BDH1281 are shown in Fig. 5(b). Both are less than 10 ms.

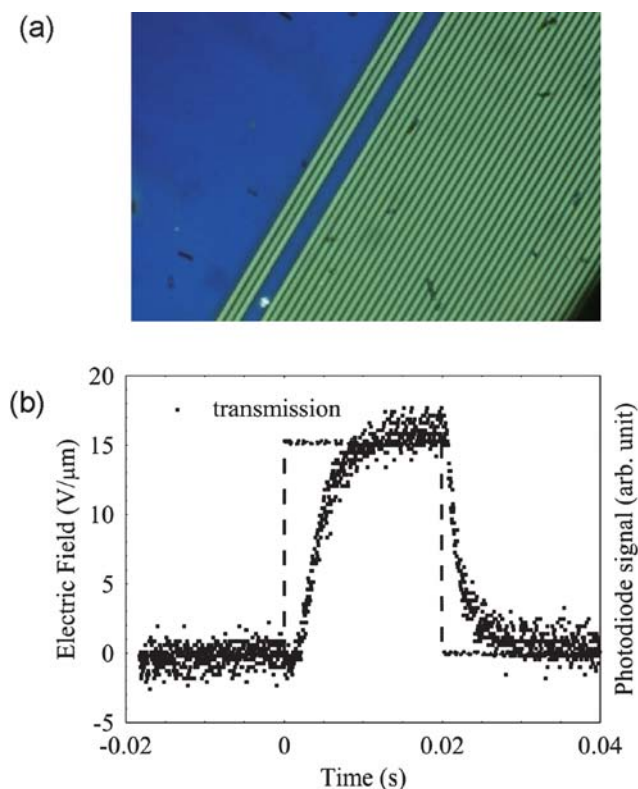


Fig. 5 Electrooptical switching of the mixture of BDH1281-doped CIPbis10BB. (a) Switching texture at 72.8°C of the mixture with 1.4 wt% BDH1281 under a sinusoidal voltage of $57 V_{p-p}$, 1 kHz: right hand side, above the in-plane electrode area (greenish yellow) and left hand side, in the area outside the electrodes. The picture represents $0.46 \text{ mm} \times 0.3 \text{ mm}$ area. The electrodes are $10 \mu\text{m}$ apart and rod-shaped dark bars are glass spacers. (b) Time dependence of the transmission between crossed polarizers in the mixture with 3.2 wt% BDH1281. A pulsed electric field of $15 \text{ V}/\mu\text{m}$ was applied at 68°C .

We also studied the EO properties in S2141 with 3.0 wt% BDH1281. Even with such low concentrations, the BPIII was easily formed and were stable until transition to the smectic phase (95.8°C BPIII 79°C SmCP_A). Fig. 6 shows the textures observed by POM with a short-wavelength-cut-off filter to prevent photodegradation. EO switching was observed at 93.5°C under an in-plane sinusoidal field of $20 V_{p-p}/\mu\text{m}$, 1 kHz. Fig. 6 (a) and (b) shows photomicrographs without and with the field, respectively. The yellow corner is the area of $10\text{-}\mu\text{m}$ spaced interdigitated electrodes, where the switching is clearly seen.

As a control experiment we also doped a calamitic LC material 6008 with BDH1281, and compared this with the doped bent-core materials. In the case of 6008, no BP phase appeared at lower BDH1281 concentrations (supporting information, Fig. S3). At concentrations higher than 5 wt% a BPI/BPII type phase with platelet textures was observed, but in a much narrower temperature range than the BPIII phase in the bent-cores. Because BPIII is usually stable at higher chirality and/or temperatures²³ than BPI or BPII, these observations show that the same chiral dopant may induce much larger chirality in bent-core (or other biaxial shape molecules¹³) than in calamitic materials.

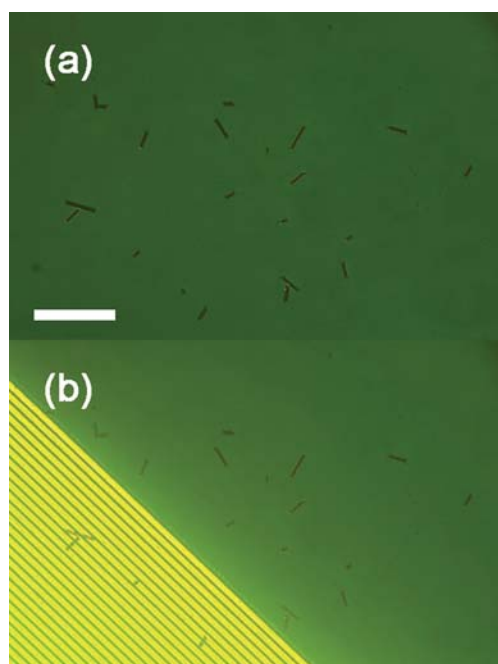


Fig. 6 Polarizing photomicrographs of the mixture of S2141 with 3.0 wt% BDH1281 taken with a short-wavelength-cut filter at 93.5 °C (a) without field and (b) under an in-plane sinusoidal field of 20 V_{pp}/μm, 1 kHz, in which the yellow corner is the area of 10 μm spaced interdigitated electrodes. The scale bar is 100 μm long.

Finally we propose that the stabilization of the amorphous BPIII phase in BCN LCs is due to the presence of smectic clusters as were recently reported based on dynamic light scattering,²⁴ C¹³-NMR,²⁵ and X-ray scattering experiments.²⁶ Most recent X-ray results on one of our studied bent-core materials (CIPbis10BB) in non-aligned²⁷ and magnetically aligned^{28,29} samples show the presence of smectic clusters in bent-core

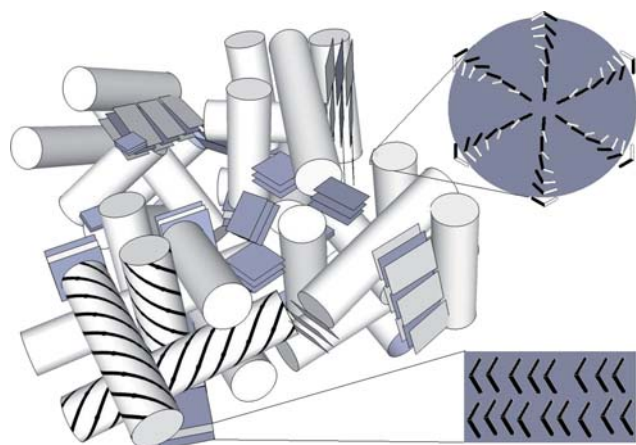


Fig. 7 Illustration of the smectic cluster-stabilized BPIII structure of BCN LCs. Cylinders with local cubic structures indicate the 3-dimensional helical structure of the bent-core molecules doped with chiral molecules, (not shown for simplicity and clarity) are broken and randomized by the smectic clusters represented by a stack of layers (grey plates). The dimensions of the sketch are roughly 0.2 μm × 0.2 μm area.

molecules that could exist in the whole nematic range including an additional 10–20 °C range in the isotropic phase. Similar X-ray analyses were performed very recently on a number of other bent-core molecules as well.^{30,31} Although macroscopic smectic blue phases are known,^{32,33} nanosize smectics clusters are not easy to form 3D twisted structures, consequently they interrupt the long-range development of the BPI or BPII lattice structures, and randomize their evolution resulting in an amorphous structure as is illustrated in Fig. 7. Combining the latest X-ray results with the flow birefringence measurements on various BCN materials²⁷ including CIPbis10BB, we estimate that the smectic clusters contain about 4–6 layers, and they are about 50–70 nm apart and thus can allow the formation of short cubic order that becomes orientationally uncorrelated after less than 0.1 μm range. These clusters can also act as walls that stop the possible macroscopic separation of the chiral molecules, explaining also the observed long term stability of the BPIII phases of BCN materials. We note that some of the largest smectic clusters could even break into twisted grain boundaries, though their small sizes probably inhibit that.

Concluding remarks

To summarize, we succeeded in stabilizing BPIII over relatively wide (~20 °C) range at low temperatures upon addition of a small amount of chiral dopant to bent-core nematic materials. Electrooptical response was also confirmed to occur in about a few to a few tens of ms response time depending on the host material and field strength. Since the phase range is limited by the nematic range of the pure BCN material, it will ultimately be necessary to make room-temperature range bent-core BP materials. This probably can be achieved by mixing several bent-core materials, as already illustrated by Nair *et al.*¹⁵ or by polymer stabilization, as done by Kikuchi *et al.*⁷ Our observations are expected to set out new display as well as optoelectronic device applications exploiting the “blue-fog” BPIII.

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