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Preliminary communication

A chiral material with a new phase sequence: twist grain boundary smectic C phase–smectic blue phases

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A new phase sequence: twist grain boundary smectic C (TGBC) to smectic blue phases (BP_{Sm}) is observed in a chiral compound (*S*)- or (*R*)-1-methyloctyl 3′-fluoro-4′-(3-fluoro-4-hexadecyloxybenzoyloxy)tolane-4-carboxylate. It is the first time that a TGBC phase has been found to occur under smectic blue phases in the absence of the twist grain boundary smectic A (TGBA) phase. These phases are characterized by polarizing optical microscopy, differential scanning calorimetry and X-ray scattering.

The discovery of the twist grain boundary A phase (TGBA phase) by Goodby *et al.* [1] in 1989 stimulated the search for such new types of material which put together chirality and smectic order. The first of them, the TGBA phase was predicted in 1988 by Renn and Lubensky [2] from an analogy, proposed by de Gennes [3], between the cholesteric to smectic A transition and the normal to superconductor transition under an external magnetic field. The TGBA theoretical structure is made of slabs of smectic A material, which are regularly stacked in a helical fashion along an axis parallel to the smectic layers. Adjacent slabs are continuously connected via a grain boundary which consists of a wall of parallel equidistant screw dislocation lines allowing helical twist. Renn and Lubensky also proposed the structure of the tilted twist grain boundary TGBC and TGBC* phases in which the smectic slabs are, respectively, SmC and SmC* [4]. The existence of the TGBC phase was demonstrated by Nguyen *et al.* [5] in 1992.

Recently, a new kind of chiral liquid crystalline phase was discovered: the smectic blue phases (BP_{Sm}), which exhibit both three-dimensional orientational order, like classical cubic blue phases, and smectic positional order. X-ray scattering experiments have revealed that one of the smectic blue phases, $BP_{Sm}2$, is not cubic, but exhibits a hexagonal symmetry [6]. The evidence of a hexagonal as opposed to a cubic symmetry proves that smectic blue phases are really new phases and not merely classical blue phases with smectic fluctuations. A model of smectic double twist cylinders which combines smectic A order and twist, not only in one direction as in TGB phases, but in the two radial directions, has already been proposed by Kamien [7]. A geometrical structure of smectic blue phases can then be sketched by packing these smectic double twist cylinders with respect to the observed symmetries. However, this model is not fully compatible with the experimental results [6]. Moreover the local smectic structure (SmC or SmA, i.e., whether the molecules are or are not tilted in the smectic layers) in the BP_{Sm} phases is not yet known. New structural elements are thus necessary to improve theoretical models. Therefore, investigations to determine what is the local smectic structure in the BP_{Sm} and also in their underlying phases can play a big role in defining these original phases.

Up to now, smectic blue phases have only been found between the isotropic liquid phase and the TGBA phase [8]. In this Communication, we report the observation of a new phase sequence Cr–SmC*–TGBC–BP_{Sm}–Iso in a chiral compound (*S*)- or (*R*)-1-methyloctyl 3′-fluoro-4′-(3-fluoro-4-hexadecyloxybenzoyloxy)tolane-4-carboxylate (simply named in the following text as 16FHFH-BTC1M8). It is the first time that smectic blue phases appear just above a TGBC phase in the absence of a TGBA phase.

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The chemical structure of the compound is given below. Apart from the length of the aliphatic chain on the asymmetric carbon, this molecule has basically the same chemical structure as those of the compounds called *n*BTMHC ($14 \leqslant n \leqslant 18$ where *n* indicates the paraffinic chain length on the benzoyloxytolane core) previously found to exhibit a TGBC–TGBA–BP_{Sm} transition [8]. Thus, this comparison with these already known *n*BTMHC compounds is carried out to prove unambiguously the new feature of the 16FHFH-BTC1M8 compound. Chemical structures of purified compounds were confirmed by IR and proton NMR. The mesomorphic properties of the new compound 16FHFH-BTC1M8 have been studied by optical polarizing microscopy, differential scanning calorimetry (Perkin Elmer 7), and X-ray scattering.

For the microscopic observations we used an Olympus BH2BHS microscope equipped with a modified Linkam THMS600 stage regulated by a LakeShore 330 temperature controller. The main features of this optical hot stage are a 0.02°C accuracy in temperature and a good control of the cooling (or heating) rate. This rate must be very low to be sure that all the phases nucleate and to obtain large monodomains: it is typically 0.001°C $\min^{-1}$. Optical observations were made on non-oriented samples placed in a plate capillary tube of 100 μm thickness between crossed polarizers.

When cooling from the isotropic phase, two smectic blue phases with detectable textures occur in a narrow temperature span: $BP_{Sm}2$ and $BP_{Sm}1$. The third smectic blue phase, called $BP_{Sm}3$, seems to have an amorphous structure like the classical BP3 [9]. Indeed, $BP_{Sm}3$ exhibits the same macroscopic symmetry as that of the isotropic phase [10]. Recent work has shown that the orientational symmetry of the $BP_{Sm}1$ phase is cubic [11] whereas $BP_{Sm}2$ exhibits a hexagonal symmetry [6]. Thus we observe a mosaic texture composed of grey birefringent platelets for $BP_{Sm}2$ and blue domains for $BP_{Sm}1$ as depicted in figure 2 on the well known compound 14BTMHC [11].

The blue colour originates from the optical activity of $BP_{Sm}1$; this can be seen in absence of high birefringence. Moreover, the BP_{Sm} lattice parameter is in the near-UV range, and is therefore too small to generate selective reflections of visible light [8]. Note in figure 3 the different texture exhibited by the new 16FHFH-BTC1M8 compound in the $BP_{Sm}1$ phase. Indeed, contrary to the 14BTMHC compound which exhibits large, smooth and homogeneous platelets, the 16FHFH-BTC1M8 texture appears frothier with the presence of ‘white lines’. Their physical meaning in the $BP_{Sm}1$ structure is not yet determined.

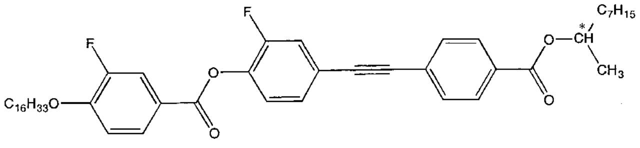

Figure 1. Chemical structure of the 16FHFH-BTC1M8 compound.

By decreasing the temperature, the TGBC phase nucleates and the transition BP_{Sm}–TGB is easily determined through the bright and coloured texture which appears. Using a prismatic cell with a planar orientation, we can identify by the Grandjean–Cano method the existence of a helical pitch in this temperature range. Quantitative pitch measurements have yet to be done. Upon cooling, the TGBC phase persists in a metastable state over a large temperature range of several degrees, preceding the SmC* phase with its classical pseudo-homeotropic and broken fan-shaped texture.

Distinguishing a TGBC from a TGBA phase by texture is very difficult. That is why X-ray scattering experiments have been carried out in LURE (Orsay, France) using synchrotron radiation. The wavelength ($\lambda = 1.45$ Å) is selected using a Ge monochromator. The incident beam is a $0.5 \times 0.5\,\mathrm{mm}^2$ spot, and it is focused on a bidimensional detector (imaging plate) located at about 350 mm from the sample. Powder samples are prepared in a 1 mm diameter Lindemann capillary tube. The calibration of the experimental set-up is made with silver behenate ($d_{001} = 58.378$ Å [12]). The capillary tube is placed vertically inside a hot stage, where the temperature is controlled within a 0.01°C accuracy. The calibration of the shift between the sample temperature (i.e., the temperature indicated by the hot stage controller) and the temperature range of the different phases observed by calorimetric and optical studies can be made using the smectic blue phases to TGB transition. At this transition, the X-ray scattering patterns change drastically: a relatively broad ring in the smectic blue phases becomes sharper in the TGB phases, as is characteristic of a quasi-long range smectic order, and its maximum intensity increases significantly [13]. Scattering patterns are recorded on cooling during the same exposure time (5 min). The wave vector *q* at the maximum intensity gives the periodicity $d = 2\pi/q$ of the smectic order. The full width at half maximum (FWHM) of the scattering peak provides an estimation of the correlation length, ζ, of the smectic order, with $\zeta = 2\pi/\mathrm{FWHM}$. The evolution of ζ through the different phases shows that at least one order of magnitude separates the isotropic liquid phase ($\zeta = 65$ Å) from the TGB phase ($\zeta > 700$ Å).

The variation of the layer spacing *d* with temperature gives a signature of the local smectic order (SmA or SmC) in the disordered smectic or TGB mesophases [5]. It reveals the existence of an average tilt of the

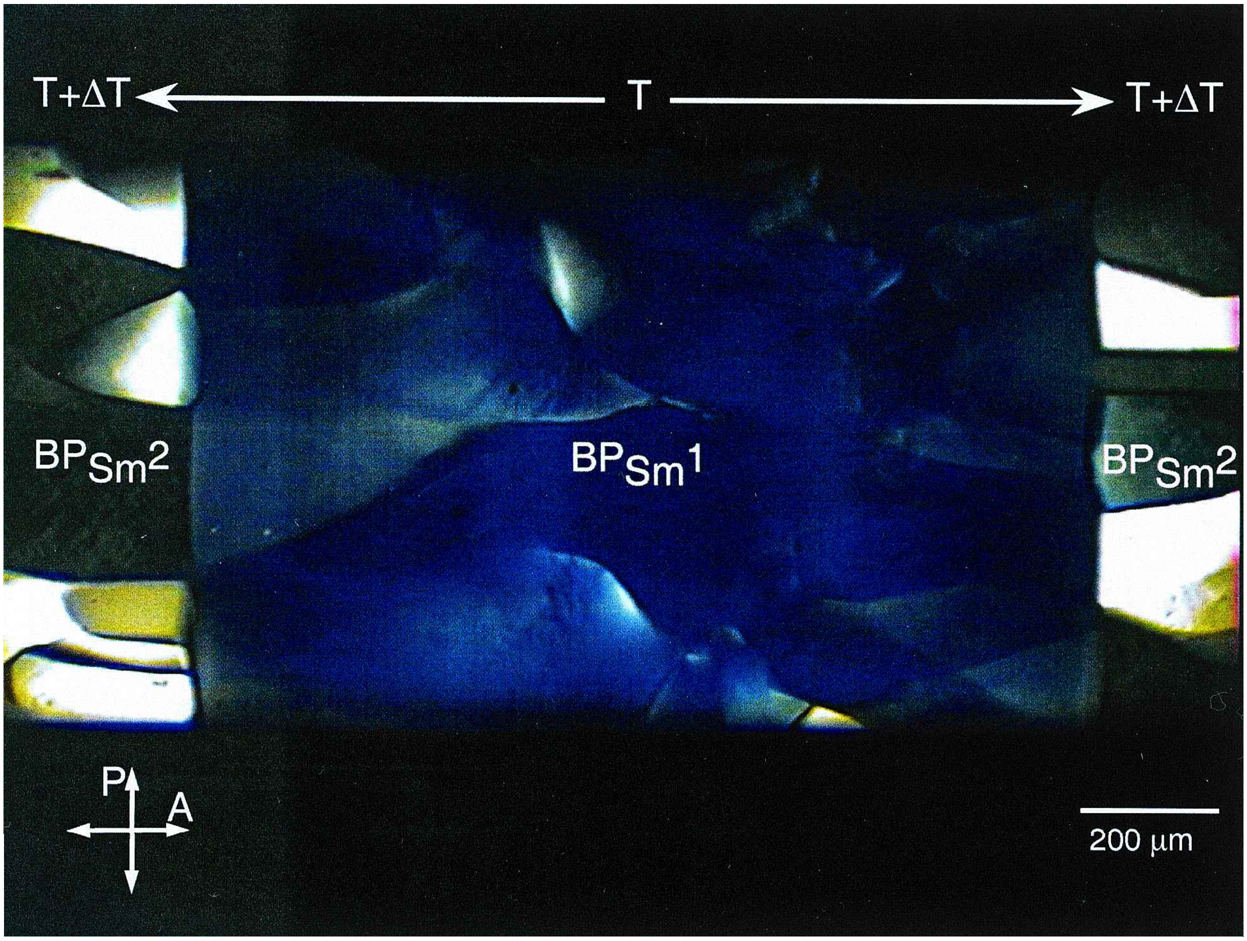

Figure 2. Coexistence of $BP_{Sm}1$ and $BP_{Sm}2$ domains (for the compound 14BTMHC with a TGBA-BP_{Sm} transition) in a flat capillary tube with a temperature gradient. These smectic blue phases are seen in transmission between crossed polarizers.

molecules with respect to the layer normal. Indeed, the effect of thermal fluctuations on the molecular orientation generates a weak decrease of the average layer spacing upon heating in the TGBA (or SmA) case. Conversely, a rise of temperature in TGBC (or SmC) phases induces an increase in fluctuations in the tilt angle of the molecular director, which leads to an increase in the average layer distance. Consequently the nature of TGB(A or C) phases can be inferred from the variations of the layer spacing versus temperature. A layer spacing increase with temperature is the signature of a local smectic C order, whereas a slight decrease indicates smectic A order.

From the isotropic phase to the smectic blue phases, the layer spacing increases continuously from roughly 39 Å to 43 Å for both the compounds 16BTMHC and 16FHFH-BTC1M8 in the same temperature range of about 4°C. This only indicates a progressive appearance of the smectic order with temperature in the BP_{Sm} phases and does not give any information on the nature of the smectic order (SmA or SmC) in the layers. Indeed, the BP_{Sm} temperature range is too short to see a variation of the smectic order, which is not a long range order. Around 67.7°C, the transition between the TGBA phase and the TGBC phase occurs for the compound 16BTMHC and an inversion of the evolution in the layer spacing versus temperature is clearly observed between these two phases as shown in figure 4.

For the new 16FHFH-BTC1M8 compound, X-ray scattering experiments unambiguously prove the absence of a TGBA phase as seen in figure 5.

This smectic C order clearly appears around 66.7°C and persists until the crystalline phase, but this evolution does not help to distinguish between a TGBC and a SmC* phase. However, the X-ray scattered intensity versus temperature, as shown in figure 6, indicates a sudden rise from about 15 000 to around 20 000 (a.u.) at the TGBC–SmC* transition, giving a temperature range of approximately 6°C for the TGBC phase upon cooling that is in good agreement with the optical observations. Figure 6 also exhibits a rise in the scattered intensity at the BP_{Sm}–TGBC transition as previously mentioned.

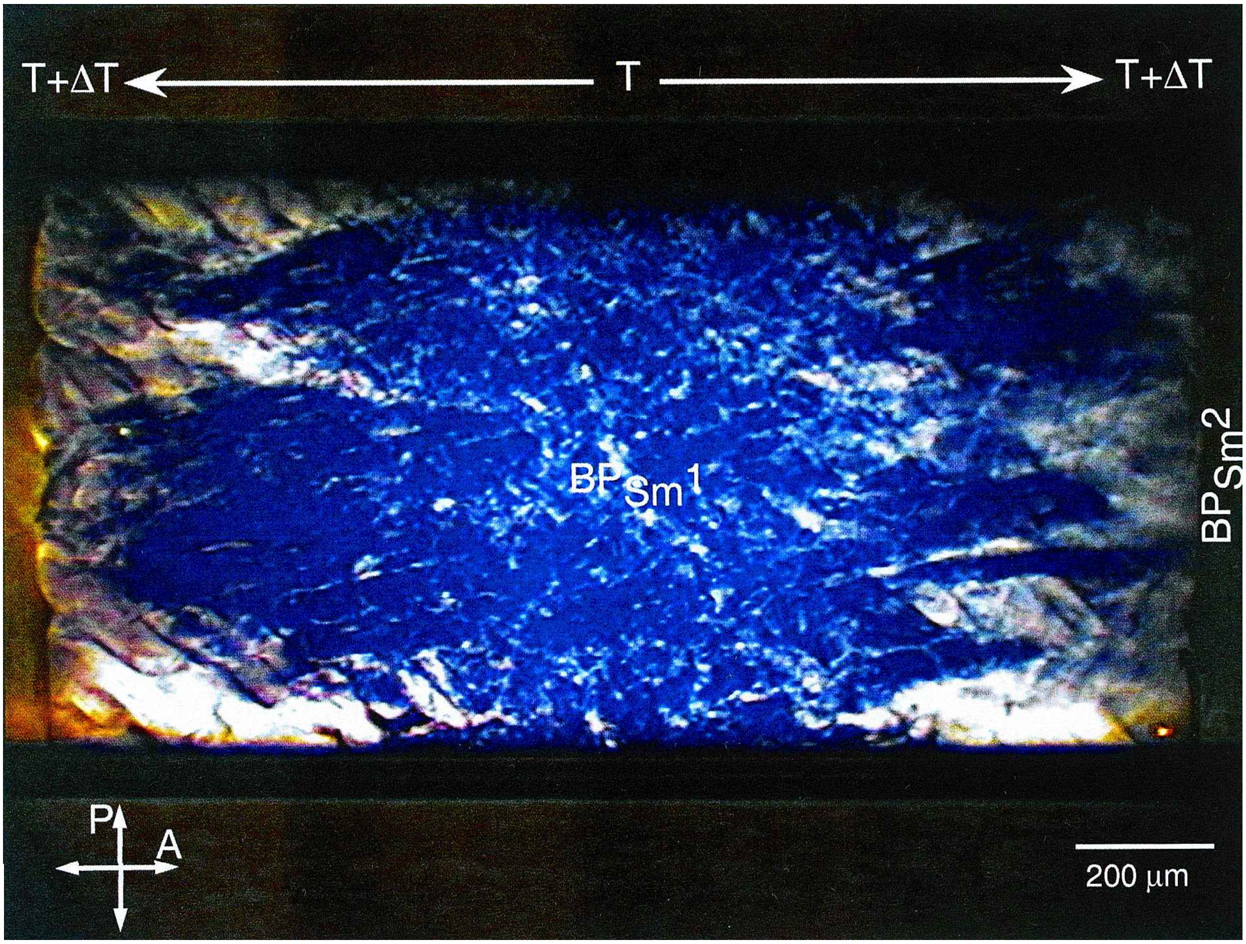

Figure 3. $BP_{Sm}1$ texture of the 16FHFH-BTC1M8 compound with a TGBC–BP_{Sm} transition. It differs from the previous cubic one (compound 14BTMHC) by having a frothier aspect. The picture is taken under similar experimental conditions to those of figure 2.

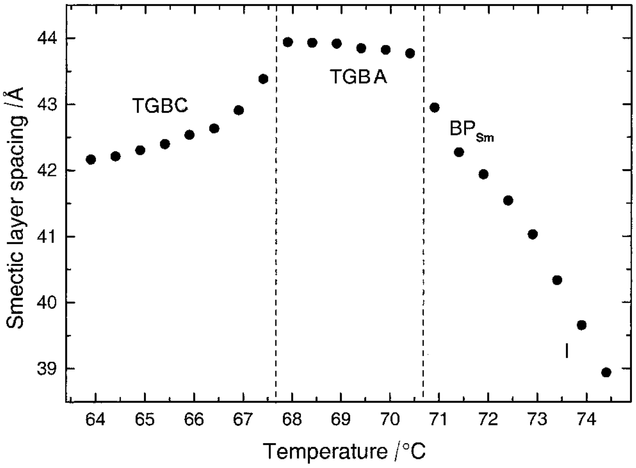

Figure 4. Evolution of the layer spacing versus temperature on the compound 16BTMHC.

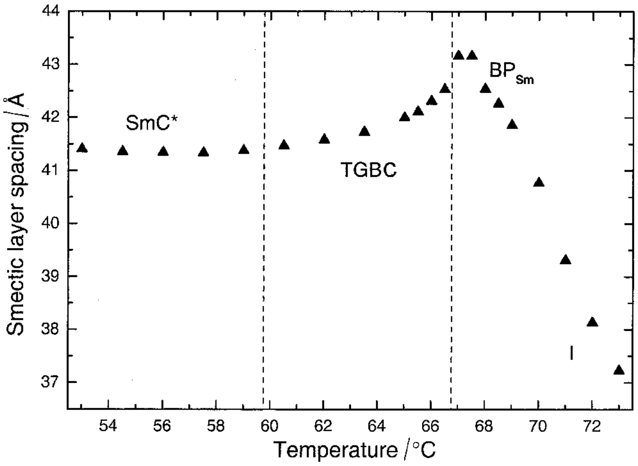

Figure 5. Evolution of the layer spacing versus temperature on the 16FHFH-BTC1M8 compound.

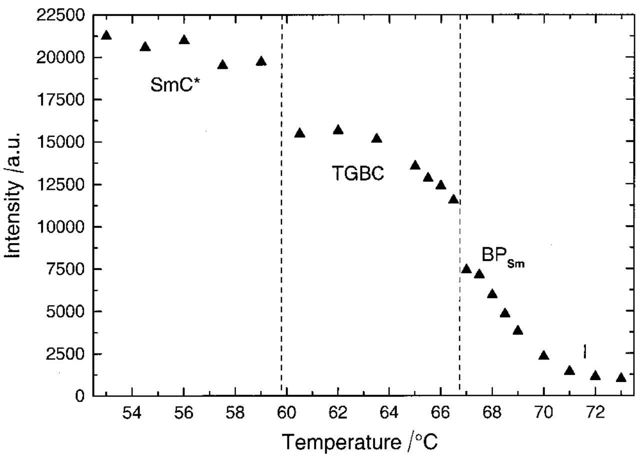

Figure 6. X-ray scattered intensity versus temperature on the 16FHFH-BTC1M8 compound.

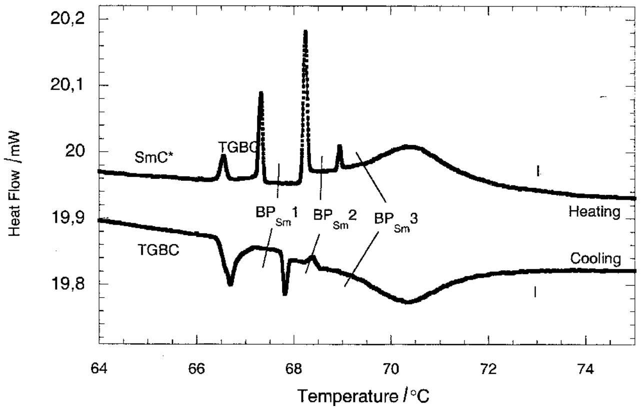

Figure 7. DSC thermograms of the 16FHFH-BTC1M8 compound on heating and on cooling at 0.2°C min^{-1}.

Note that the SmC*–TGBC transition appears in figure 7 in the DSC thermogram performed on heating, but has no signature on cooling as already observed for the 16BTMHC compound [8].

Thus the thermodynamically stable TGBC phase actually exists in a narrow temperature range on heating (< 1°C), whereas upon cooling the TGBC phase persists over a larger temperature span of several degrees (> 5°C) in a supercooled state.

By this communication, we report the first observation of a TGBC–smectic blue phases phase sequence. We have not yet determined the BP$_{Sm}$1 structure, but first insights, such as the observed textures, suggest that the structure of this phase is dependent on the nature of the underlying TGB state. Further X-ray scattering investigations on BP$_{Sm}$ monodomains are in progress.

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