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A Chiral, Incommensurate Helical Phase in a Smectic of Achiral Bent-Core Mesogens

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An achiral, bent-core mesogen forms several tilted smectic liquid crystal phases, including a non-polar, achiral de Vries smectic A which transitions to a chiral, ferroelectric state in applied electric fields above a threshold. At lower temperature, a chiral, ferroelectric phase with a periodic, supermolecular modulation of the tilt azimuth, indicated by a Bragg peak in carbon-edge resonant soft X-ray scattering, is observed. The absence of a corresponding resonant Umklapp peak identifies the superlayer structure as a twist-bend-like helix that is only weakly modulated by the smectic layering.

The discovery of spontaneous macroscopic polar ordering [1] and chirality [2] in fluid smectic liquid crystal phases of achiral bent-core mesogens has led to the exploration of a rich family of novel liquid crystal phases and self-assemblies [3–7] in which the key macroscopic elements of polarity, chirality, and smectic layering all appear as spontaneously broken symmetries. While the smectic layer-scale order of bent-core mesogens, resulting from strong intralayer coupling between molecular tilt and polarity, is quite well characterized, superlayer structuring beyond that of the four basic SmCP bilayer phases combining synclinic or anticlinic tilt with ferroelectric or antiferroelectric polarity [2], as sketched in Supplemental Figure S1, have not been definitively identified. Possible superlayer structures analogous to those seen in tilted SmC* phases of chiral, rod-shaped molecules could be incommensurate or commensurate with the underlying smectic layer spacing and feature states of varying azimuthal orientation of the molecular long axis about the layer normal, z , such as the chiral helical precession along z with equal, discrete orientational jumps between layers of the SmC* phase and the ferroelectric phases with periodic arrays of discrete jumps of different sizes [35].

Since the period of such superlayer structures, p , can be as short as two layers, the structural study of such phases requires the effective probing of molecular orientation at the nanoscale. This can be achieved using resonant X-ray scattering, a technique sensitive to atomic environment [9–19] that has previously enabled the discovery and definitive characterization of superlayer organization in several SmC* phases and sub-phases, employing the K-edge resonance of atoms incorporated in the liquid crystal molecule [9, 11].

Several recent observations suggest the possibility of chiral superlayer ordering in achiral bent-core mesogens: Takahashi et al. have identified such a structure in a SmCP phase of a bent-core mesogen doped with a chi-

ral, rod-shaped molecule that as a neat material exhibits SmC* _{α} and ferroelectric phases [20]; Abberley et al. have reported a superlayer helix in a smectic phase of bent dimers of molecular rods [21]; Panarin and co-workers have recently proposed, based on AFM evidence, the existence of tilted, helical supermolecular ordering in several achiral bent-core mesogens with 4-cyanoresorcinol bisbenzoate cores [22]. Earlier investigations of this molecular family had concluded, however, that their polar phases were orthogonal, i.e., untilted and therefore not chiral [23, 24]. Motivated by these conflicting reports and the ongoing interest in the chiral sub-phases of liquid crystals, we have studied one of the members of this homologous series, **PAL30**, which has $n = 14$ alkyl tails (see Figure 1(a)). Our experiments, using non-resonant X-ray scattering (SAXS), resonant soft X-ray scattering (RSoXS), electro-optic techniques, and polarized light microscopy (PLM), summarized in Figure 1, reveal an exotic phase sequence, including an achiral de Vries smectic which becomes chiral in sufficiently large applied electric fields, and, at lower temperature, a tilted, chiral smectic with superlayer helical ordering.

X-ray scattering from **PAL30** is shown in Figures 1(b) and S3. Upon cooling from the isotropic, a single, non-resonant SAXS peak appears at 175 °C, at a wavevector q_0 corresponding to Bragg scattering from the smectic layers in the Sm1 phase with spacing $d_0 = 2\pi/q_0 = 48 \text{ \AA}$. The layer spacing increases slightly on cooling to the crystal phase at 65 °C and is consistently smaller than the calculated molecular length, $l = 59.9 \text{ \AA}$, throughout this temperature range, suggesting that the molecules are tilted in all of the smectic phases, to first order by an average amount estimated using $\theta_{\text{xray}} = \cos(d_0/l)$ of 33° (see Figure S4). In the Sm1 temperature range (110 °C $\leq T \leq 175$ °C), there are no RSoXS scattering features that would indicate a superlayer periodic structure (see Figure S2 and the Supplemental video).

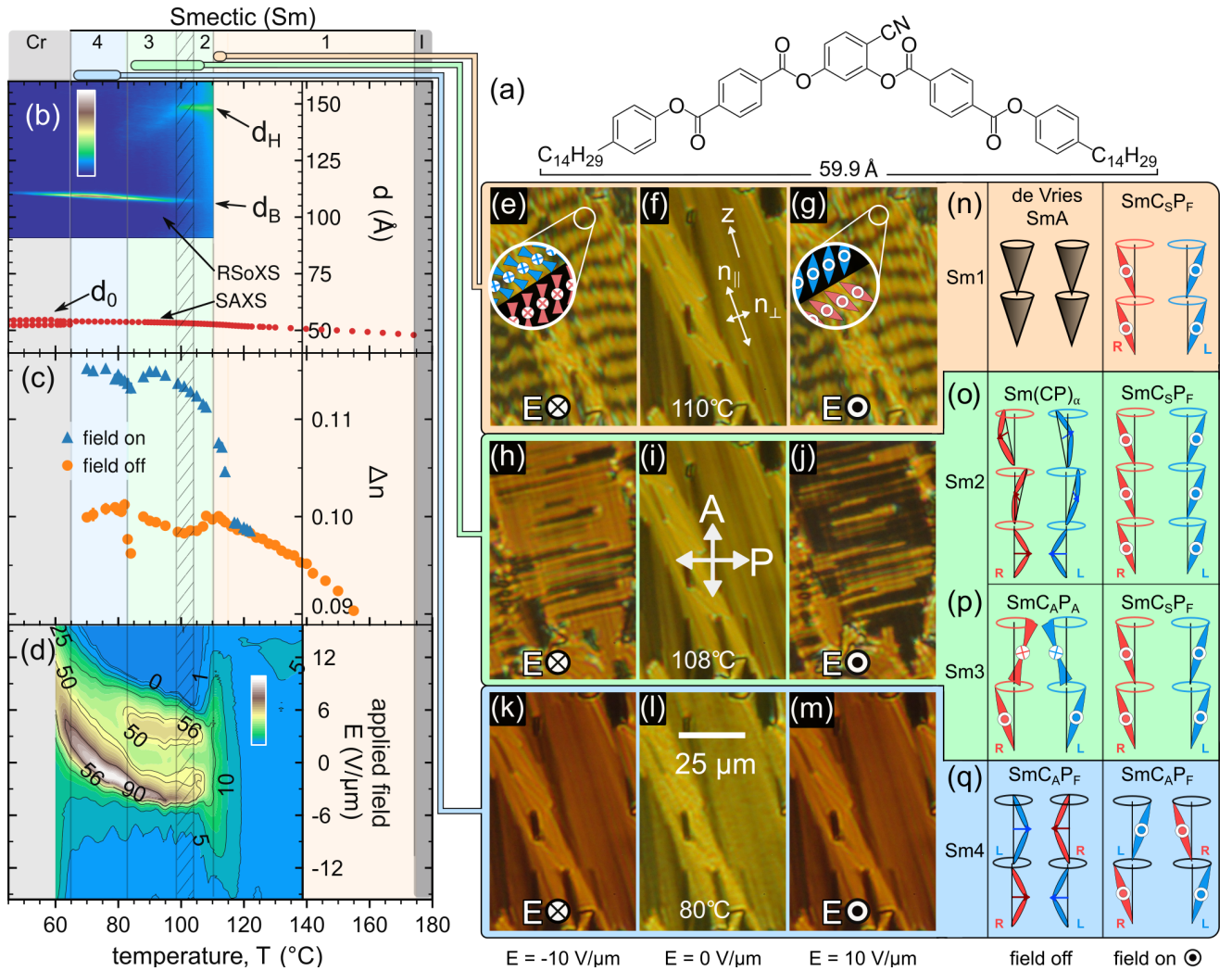


FIG. 1. Experimental characterization of **PAL30**. (a) The **PAL30** molecule, showing the all-trans length calculated using the program Spartan. (b–d) Phase properties vs. temperature. The solid vertical lines denote phase boundaries and the cross-hatching phase coexistence. (b) SAXS shows the smectic layer spacing in all phases to be $d_0 \approx 48 \text{ \AA}$. Resonant carbon K-edge reflections are from superlayer modulations of the molecular orientation about the layer normal z , the peak at $d_H \approx 150 \text{ \AA}$ corresponding to the pitch of the incommensurate, helical precession in the Sm2 phase, and at $d_B = 2d_0$ to the bilayer ordering of the Sm3 and Sm4 phases. (c) Birefringence of planar-aligned cells with layers normal to the plates, with and without applied electric field ($E = 20 \text{ V}/\mu\text{m}$). (d) Polarization current (in nA) in response to a triangle-wave applied electric field: a single-peak, Langevin-like response at lower temperatures in the Sm1 phase; a triple peak in the Sm2 phase, associated with ferroelectric switching[25] and indicative of helical unwinding[35], coalescing into a double peak in the Sm3, indicating a non-polar ground state at $E = 0$; and a single current peak in the Sm4 phase caused by the block polarization switching of the ferroelectric SmC_AP_F ground state. (e–m) Characteristic optical textures in a planar cell, viewed between crossed polarizers. The $E = 0$ textures are focal conics typical of a fluid smectic with an optic axis along z . Field application induces chiral, tilted conglomerate domains (of opposite handedness) in the Sm1–Sm3 phases, but only a change in birefringence in the Sm4. (n–q) Proposed superlayer structure of **PAL30** phases, with and without applied electric field: (n) Sm1: achiral de Vries-like SmA \rightarrow chiral SmC_SP_F ; Sm2: superlayer chiral helix \rightarrow chiral SmC_SP_F ; Sm3: superlayer chiral bilayer $\text{SmC}_A\text{P}_A \rightarrow$ chiral SmC_SP_F ; Sm4: SmC_AP_F with \mathbf{P} parallel to the glass \rightarrow SmC_AP_F with \mathbf{P} normal to the glass.

At the transition to the Sm2 phase, at 110°C , marked by a distinct enthalpy peak in the DSC (Figure S5), a single, sharp resonant peak appears at $q_H = 0.042 \text{ \AA}^{-1}$, corresponding to a molecular orientational structure with a period $d_H = 148 \text{ \AA} \approx 2.8d_0$ that is incommensurate with the smectic layer spacing (Figure 2(b)). Below 104°C , this

reflection becomes weaker and another sharp, resonant reflection at higher q grows in, the coexistence indicating a first-order transition to the Sm3 phase. This second Bragg peak, which persists down to the crystal phase, has a wavevector $q_B \approx q_0/2$, indicative of a commensurate, bilayer orientational structure in the Sm3 and Sm4 phases.

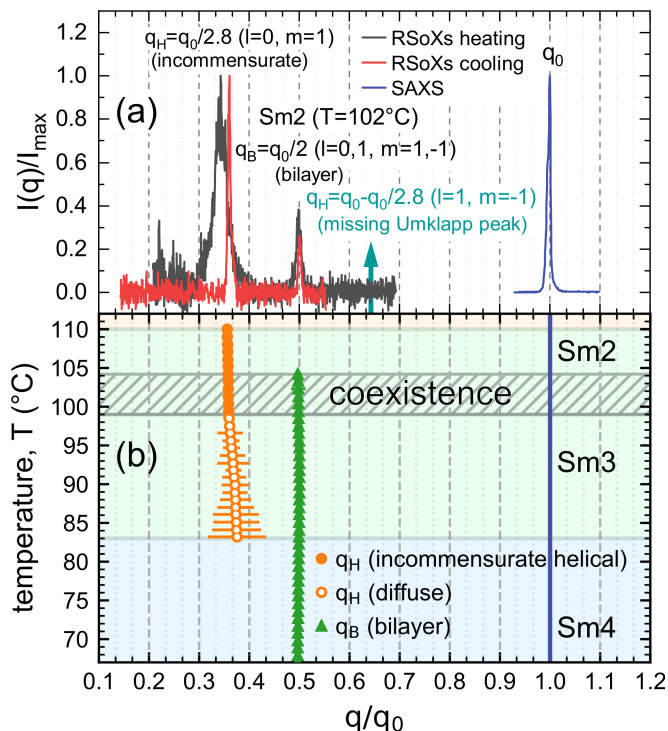


FIG. 2. X-ray scattering from **PAL30**. (a) SAXS gives a peak from the smectic layer ordering at $q = q_0$. The RSoXS peak at q_H indicates that there is superlayer orientational ordering with periodicity d_H in the Sm2 phase. In general, superlayer orientational modulation in a smectic generates RSoXS peaks at wavevectors along the layer normal at $q(l, m) = l(2\pi/d_0) \pm m(2\pi/d_H)$ [10]. The observation of an RSoXS reflection at $q = q(0, 1)$ and the absence of an Umklapp peak at $q = q(1, -1)$ in the Sm2 confirms a superlayer helix with a scattering amplitude modulation due to the smectic layering that is undetectably weak. (b) Temperature dependence of resonant scattering. The helix peak at $q_H \approx 1/(2.8d_0)$ becomes diffuse in the Sm3 phase. Splitting of the bilayer peak at q_B , which would indicate helical precession of the bilayer structure, is not observed.

Below 99°C , the incommensurate peak broadens dramatically and moves to higher q , indicating the presence of short-ranged, Sm2-like helical fluctuations persisting in the Sm3 phase, and disappears at the transition to the Sm4 phase at 83°C . The Sm4 phase exhibits only the bilayer RSoXS reflection at q_B .

The RSoXS scattering from a single layer can be analyzed, following Levelut and Pansu, in terms of a monoclinic second-rank tensor with a principal axis tilted from and then azimuthally rotated about the layer normal [10, 13, 14]. Scattering from a stack of such layers is calculated by summing over the contributions of the individual layers at different z . Resonant scattering peaks from azimuthally periodic arrangements are found at wavevectors along z , $q(l, m) = l(2\pi/d_0) \pm m(2\pi/p)$, where p is the pitch. In principle, resonant scattering should appear at all values of l (harmonics of q_0), and

at values of $m = 0, \pm 1, \pm 2$ that depend on the superlayer structure. In an incommensurate, helical structure, like the SmC $_\alpha$ phase, only the fundamental and harmonic peaks at $q(l = 0, m = +1, +2)$ and the Umklapp peaks at $q(l = +1, m = -1, -2)$ are found in the range $0 < q(l, m) < q_0$. If the resonant scatterers are confined to lie precisely on layers spaced by d_0 , then the intensities of these peaks will be identical [10]. Out-of-layer molecular positional fluctuations, and, in particular, those for which there is a coupled azimuthal orientation that keeps the molecule on the helix, $\delta\phi = (2\pi/p)\delta z$, reduce the intensities of the resonant harmonic peak at $2q_H$ and of the Umklapp peaks at $q_0 \pm q_H$, relative to that of the fundamental at q_H [10]. In our RSoXS scans of these peaks, only the fundamental is seen above the background, so that only the upper limit of the intensity ratio of the Umklapp and fundamental peaks can be estimated. From the RSoXS heating scan of Figure 2(a), we find $I_U/I_F \lesssim 0.03$, implying a very weak fractional modulation of the density of helical scatterers, ρ , due to fluctuations in the smectic layering $\sqrt{\langle \delta\rho^2 \rangle} / \rho_0 < 0.17$. The absence of the harmonic peaks places a similar limit on how much the density modulation of helical scatterers deviates from being purely sinusoidal.

The optical textures of planar-aligned (bookshelf) cells of **PAL30** were studied using PLM. Upon cooling from the isotropic, the Sm1 phase grows in (at 175°C) as bâtonnets, giving a smooth, focal-conic texture typical of an orthogonal fluid smectic (Figure 1(f)). However, given the large value of the estimated molecular tilt, θ_{xray} , the Sm1 is probably a de Vries smectic. In planar-aligned cells, there is no observable field-induced change of the in-plane birefringence, $\Delta n = n_{\parallel} - n_{\perp}$, in small applied electric fields (Figure 1(f)), or in the optic axis orientation, θ_{opt} (Figure 3).

Below 115°C , a threshold field, E_{th} , above which a first-order structural change marked by the appearance of chiral conglomerate domains occurs, becomes experimentally accessible. These domains are polar and exhibit a uniform, saturated optic axis tilt on the order of $\theta_{\text{opt}} \approx 18^\circ$ from the layer normal, implying that the achiral, untilted Sm1 phase transforms in the field to a B2-like, homochiral SmC $_S$ P $_F$ state (Figure S1(c)) [26]. The field-induced left- and right-handed domains form a “tiger stripe” pattern (Figures 1(e,g)). The local domain handedness in this unusual conglomerate texture is apparently locked in after the first few field cycles. This bias is due to a chiral memory effect at the surface since, as Figures 1(d) and 3 show, the sub-threshold bulk state has an achiral field response, with a linear polarization current (implying $P \propto E$) and no detectable reorientation of the optical tilt. E_{th} decreases strongly on cooling as the transition to the Sm2 phase is approached, as shown in the inset of Figure 3.

In the lower part of the Sm1, and throughout the Sm2, Sm3 and Sm4 phases, the birefringence increases on appli-

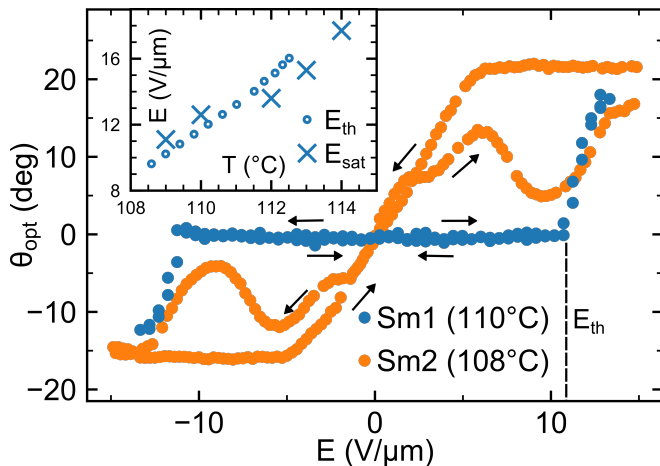


FIG. 3. Optical tilt of **PAL30** vs. applied field. The Sm1 phase shows no electrooptic response in weak fields $E < E_{th}$. Fields $E > E_{th}$ induce an electroclinic tilt and result in the formation of chiral domains. E_{th} , which becomes smaller with decreasing T (inset), matches closely E_{sat} , the field at which the induced polarization saturates, extracted from Figure 1(d). The Sm2 phase exhibits a chiral electroclinic effect near $E = 0$ and hysteresis in the field-induced helix unwinding to the SmC_5P_F state.

cation of an electric field, as seen in Figure 1(c), changing from yellow to orange. Measurements of Δn at $E = 0$ and $E = 20 \text{ V}/\mu\text{m}$ (Figures 1(c) and S6), show that the birefringences in the lower temperature phases with and without an applied field are of the order of $\Delta n_{on} \sim 0.12$ and $\Delta n_{off} \sim 0.10$. Assuming that the field-on SmC_5P_F state (Figures 1(n-p) and S1) gives a uniform director orientation with the optic axis in the plane of the cell, then $\Delta n \sim 0.12$ would correspond to the maximal birefringence $n_3 - n_1$ of the SmC_5P_F state. Modeling the bent-core molecule as two uniaxial, birefringent rods connected with an opening angle of Ψ , and tilting this molecule from z by an angle θ , we have calculated the birefringence of all of the states shown in Figure 1. If the Sm1 phase is assumed to be a de Vries SmA, with azimuthally averaged molecules distributed on a tilt cone of angle θ , the best fit to the measured birefringence values Δn_{on} and Δn_{off} is obtained with $\Psi = 150^\circ$ and $\theta = 15^\circ$. The calculated birefringence as a function of temperature is shown in Figure S6.

The transitions between the smectic phases are difficult to see when $E = 0$ because they are all orthogonal in appearance, with an optic axis along z , and have similar birefringence. At the transition from Sm1 to the Sm2 phase, however, arbitrarily small electric fields induce molecular tilt in the (Figure 3), leading to the formation of optically distinct, conglomerate chiral domains with opposite tilt (Figures 1(h-j)), again corresponding to a field-induced transition to a SmC_5P_F state. The birefringence and orthogonal appearance of the Sm2 ground state are consistent with the helical superlayer structure

indicated by RSoXS.

The texture and birefringence of the Sm3 phase in the absence of field are consistent with the SmC_AP_A bilayer structure indicated by RSoXS. The field-induced conglomerate domain morphology in both the Sm2 and Sm3 phases is distinct from that of the undulating Sm1 tiger stripes, with straight domain boundaries that tend to form parallel to the layers, as in an antiferroelectric calamitic being driven to a ferroelectric state [27]. The optical tilt in these domains is found to be $\theta_{opt} \sim 18^\circ$.

The response to applied field changes dramatically again at the transition from Sm3 to Sm4, with no visible brush rotation or evidence of domain formation at any E . The birefringence in the Sm4 phase increases continuously with field, saturating at a value comparable to that observed in the field-induced Sm2 and Sm3 conglomerate domains.

The polarization current, measured with a triangular applied field, is shown vs. temperature in Figures 1(d) and S7-S9. Upon cooling from the isotropic, a single current bump centered about $E = 0$ first appears at lower temperatures in the Sm1 phase, indicating a Langevin-type field-induced orientation of \mathbf{P} , with a linear response near $E = 0$ and the current vanishing when \mathbf{P} becomes saturated (for $E \geq E_{sat}$). Significantly, E_{sat} is similar in magnitude to E_{th} , the threshold field required for the Sm1 transition to chirality observed optically (Figure 3, inset), indicating that the field first orders the Langevin system of initially azimuthally random molecular polarizations, with the Sm1 remaining in an achiral state, and that the phase becomes chiral only at higher fields, once \mathbf{P} is saturated (Figure S10). Upon entering the Sm2, this polarization bump splits into three peaks roughly centered about $E = 0$ that evolve to two peaks on cooling through the Sm3. **PAL30** thus transforms on cooling from the non-polar Langevin ground state of the Sm1, where $P = 0$ is enforced by entropy, to energetically stabilized ground states in which the spatial average of $\mathbf{P}(\mathbf{r})$ in the absence of applied field is also zero: the incommensurate helical winding of the polarization in the Sm2, and the antiferroelectric bilayer structure in the Sm3. At the transition to the Sm4, a single current peak dominates, characteristic of the block polarization switching of a ferroelectric ground state that is surface-stabilized with \mathbf{P} parallel to the cell plates at $E = 0$, such as occurs in the orthorhombic SmAP_F phase [28]. The absence of brush rotation during the field-induced reorientation of the polarization in Sm4 is consistent with achiral SmC_AP_F superlayer organization.

In summary, X-ray and optical experiments show that **PAL30**, an achiral, bent-core mesogen, forms smectic liquid crystal phases with the molecules substantially tilted from the layer normal, with phase sequence: $I \xrightarrow{175^\circ\text{C}}$ de Vries SmA $\xrightarrow{110^\circ\text{C}}$ $\text{Sm}(\text{CP})_\alpha \xrightarrow{99^\circ\text{C}}$ $\text{SmC}_A\text{P}_A \xrightarrow{83^\circ\text{C}}$ $\text{SmC}_A\text{P}_F \xrightarrow{65^\circ\text{C}}$ Cr.

The highest temperature phase exhibits short-ranged ordering of the tilt azimuth that is decoupled from the molecular polarization, forming a uniaxial, non-polar,

achiral de Vries smectic A. An applied electric field of increasing magnitude continuously aligns the initially random polarization and the phase acquires orthorhombic symmetry. The field eventually saturates the polarization orientation, inducing a transition to a tilted, chiral, ferroelectric smectic state. Upon cooling, a novel chiral, ferroelectric phase which we call the $\text{Sm}(\text{CP})_\alpha$ appears. This phase is similar to the SmC_α phase of chiral, rod-shaped molecules [9, 11, 12, 16], but with the chirality appearing here as a broken symmetry. A periodic azimuthal precession of the director about the layer normal that is incommensurate with the smectic layering is confirmed by the presence of Bragg reflection peaks in carbon-edge resonant soft X-ray scattering. The absence of the corresponding resonant Umklapp peak unambiguously identifies this structure as a helical modulation of the orientational ordering in which molecules exhibit substantial coupled rotational/positional out-of-layer fluctuations, forming a twist-bend-like helix.

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Further experimental details and additional figures are provided in the Supplemental Materials [29].

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