We report the observation of the smectic A\textsubscript{f}, a liquid crystal phase of the ferroelectric nematic realm. The smectic A\textsubscript{f} is a phase of small polar, rod-shaped molecules that form two-dimensional fluid layers spaced by approximately the mean molecular length. The phase is uniaxial, with the molecular director, the local average long-axis orientation, normal to the layer planes, and ferroelectric, with a spontaneous electric polarization parallel to the director. Polarization measurements indicate almost complete polar ordering of the $\sim10$ Debye longitudinal molecular dipoles, and hysteric polarization reversal with a coercive field $\sim2 \times 10^5$ V/m is observed. The SmA\textsubscript{f} phase appears upon cooling in two binary mixtures of partially fluorinated mesogens: 2N/DIO, exhibiting a nematic (N)–ferroelectric SmN\textsubscript{IA} (SmFA)–ferroelectric nematic (N\textsubscript{f})–SmA\textsubscript{f} phase sequence, and 7N/DIO, exhibiting an N–SmZ\textsubscript{A}–SmA\textsubscript{f} phase sequence. The latter presents an opportunity to study a transition between two smectic phases having orthogonal systems of layers.

Proper ferroelectricity in liquids was predicted in the 1910s by P. Debye (1) and M. Born (2), who applied the Langevin–Weiss model of ferromagnetism to propose a liquid-state phase change in which the ordering transition is a spontaneous polar orientation of molecular electric dipoles. A century later, in 2017, two groups independently reported, in addition to the typical nematic (N) phase, novel nematic phases in strongly dipolar mesogens, the “splay nematic” in the molecule RM734 (3–5), and a “ferroelectric-like nematic” phase in the molecule DIO (6). These nematic phases were subsequently demonstrated to be ferroelectric in both RM734 (7) and in DIO (8, 9) and to be the same phase in these two materials (9). This new phase, the ferroelectric N (N\textsubscript{f}), is a uniaxially symmetric, spatially homogeneous, N liquid having $\geq90\%$ polar ordering of its longitudinal molecular dipoles (7, 9). A related new phase recently observed is the helical N\textsubscript{f} (10–14), obtained by chiral doping of RM734, DIO, or their homologs or by introducing chiral tails into the molecular structures (15). DIO also exhibits an additional phase, found between the N and N\textsubscript{f} (6), which we have recently characterized, terming it the smectic Z\textsubscript{A} (16) and showing it also to be new: a density-modulated antiferroelectric exhibiting lamellar order with $\sim18$ nm repeats, comprising pairs of $\sim9$-nm-thick layers with alternating polarization, the director and polarization being oriented parallel to the layer planes.

Here, we introduce another phase of the N\textsubscript{f} realm, a uniaxial, lamellar phase with the director normal to the layers and a spontaneous polarization along the director, which we have termed the SmA\textsubscript{f} (17, 18). Schematic drawings of the phases discussed here, sorted into macroscopically nonpolar and polar types, are shown in Fig. 1, along with the molecular structures and phase sequences of the mesogens used in the mixtures. The macroscopically nonpolar, paraelectric N and smectic A (SmA) phases, the N\textsubscript{f} and ferroelectric SmA (SmA\textsubscript{f}) phases, and the antiferroelectric SmZ\textsubscript{A} phase are sketched in Fig. 1A, the light-to-dark shading of the schematic molecules indicating their dipolar symmetry. The SmA\textsubscript{f} phase is observed in 50:50 wt% AUUQ2N/DIO (2N/DIO) and AUUQ7N/DIO (7N/DIO) mixtures. The region of Fig. 1A shaded yellow shows the generic phase sequence observed in the mixtures on cooling (Iso $\rightarrow$ N $\rightarrow$ SmZ\textsubscript{A} $\rightarrow$ N\textsubscript{f} $\rightarrow$ SmA\textsubscript{f} $\rightarrow$ X), noting that some phases may be missing in a given component or mixture. For example, none of the single components exhibits the SmA\textsubscript{f} phase, and the 7N/DIO mixture does not have the N\textsubscript{f} phase. The first mesophase that appears on cooling any of the components and mixtures from the isotropic is the conventional dielectric N phase, which, in the present context, is also considered paraelectric. They all cool from the N into the antiferroelectric smectic Z (SmZ\textsubscript{A}) (16) phase.

The 2N/DIO mixture then transitions first to the N\textsubscript{f} phase and then, on further cooling, to the SmA\textsubscript{f}, while 7N/DIO goes directly to the SmA\textsubscript{f}. This enables a comparative study of the N\textsubscript{f} $\rightarrow$ SmA\textsubscript{f} and SmZ\textsubscript{A} $\rightarrow$ SmA\textsubscript{f} transitions, the latter entailing the simultaneous disappearance of the SmZ\textsubscript{A} layering parallel to the director and the formation of the SmA\textsubscript{f} layering normal to the director, in the absence of any director/polarization reorientation.
In contrast to the conventional dielectric SmA phase, the SmAF phase exhibits a macroscopic polarization $P$, with the polarization in every layer pointing in the same direction, along the director, $n$, normal to the layer planes. The phase is uniaxial and has a high degree of polar order ($P > 0.9$). Domains of opposite polarization separated by polarization-reversal walls (sketched in Fig. 1A) are observed in regions with continuous smectic layering.

This ferroelectric phase is distinct from the phases previously described in several families of uniaxial “polar smectics”, including the monolayer paraelectric SmA$_1$, the partial bilayer SmA$_d$, the antipolar bilayer SmA$_2$ phase, and a variety of polarization-modulated phases (SmA, SmC, SmC$_2$, etc.) of dipolar molecules (19–21), in that these all have zero net average polarization (22).

Results

X-Ray Scattering. We have previously carried out X-ray diffraction, polarized light microscopy, and polarization measurement studies of the single molecular components, DIO (9, 16) and 2N,7N (20, 29), and in the mixtures 2N/DIO and 7N/DIO (29–31). All of our observations indicate that the SmA, SmA$_d$, and SmA$_f$ phases observed in these different materials: the SmA$_d$ variety and that the observed electrical effects were manifestations of bilayer antiferroelectricity. The SmA$_f$ is also different from the orthogonal polar smectic phases exhibited by some bent-core mesogens, which form biaxial smectics with the spontaneous polarization oriented parallel to the smectic layers (26–28).

Fig. 1. Structures, phase sequences, and schematic of the liquid crystal phase behavior of 2N, 7N, and DIO single components and their indicated mixtures. (A) The relevant phases of rod-shaped molecules with on-axis electrical dipole moments, where the dipole direction of each schematic molecule is indicated by its black-to-green shading, grouped into macroscopically nonpolar and polar types. The experiments reported here confirm the existence of the previously described paraelectric nematic (N) (3, 4), antiferroelectric smectic Z (SmZA) (16), and ferroelectric nematic (NF) (4–7) phases, as well as the new SmA$_f$ phase. These phases appear upon cooling in the general order indicated in the yellow-shaded area. Note that the N$_p$ phase is missing in the 7N/DIO mixture, allowing for a direct smectic ZA to smectic AF transition. The solid, heavy lines depict smectic layering. The SmA$_f$ phase is spontaneously ferroelectric, with polarization $P \sim 6 \mu C/cm^2$ and polar order parameter $P > 0.9$, values comparable to those of the N$_p$ phase of DIO (6) and RM734 (7). Polarization reversal is mediated by the motion of pure polarization reversal domain walls (heavy, dashed line). The antiferroelectric layer-by-layer alternation of polarization induces splay modulation of the director in the SmZA phase, but splay is suppressed in the ferroelectric N$_p$ and SmA$_f$ phases. (B) Structures and phase sequences of the liquid crystals and their mixtures studied here.
nematics with a macroscopic polarization along the nematic director, and the SmZA is the same bilayer antiferroelectric phase in all of the components and mixtures, with a layer spacing $d_{M} \sim 90 \text{ Å}$ in DIO, $d_{M} \sim 81 \text{ Å}$ in the 2N/DIO mixture, and $d_{M} \sim 60 \text{ Å}$ in the 7N/DIO mixture. The period of the layer-by-layer antiferroelectric polarization alternation is $2d_{M}$.

In this study, we describe the liquid crystal (LC) behavior of the 50:50% 2N/DIO and 7N/DIO mixtures, both of which exhibit the SmA$_{F}$. We find that these mixtures show (i) similar scattering in the SmA$_{F}$ phase from the SmA$_{F}$ layering, with a fundamental SmA$_{F}$ Bragg scattering peak at $q_{||} = (q_{||}/A_{F})n$, indicating layer spacing close to the mean molecular length; (ii) similar intense diffuse scattering in all of the phases (N, SmA$_{F}$, N$_{F}$, and SmA$_{P}$) peaked at the SmA$_{F}$ layer Bragg scattering peak position, indicating head-to-tail molecular positional correlations; (iii) no indication of a tendency for polar SmA$_{F}$ antiferroelectric bilayer ordering, i.e., no sharp or diffuse scattering feature at $q_{||} = (1/2q_{||}/A_{F})$; (iv) similar uniaxial birefringence; (v) similar SmA$_{F}$-like optical textures; (vi) similar response of the SmA$_{F}$ to surface alignment conditions and applied electric field; and (vii) similar polarization reversal dynamics in the SmZA$_{F}$ phase and in the SmA$_{F}$ phase. We discuss the two mixtures separately because of the differences in how the SmA$_{F}$ grows in on cooling, 2N/DIO coming from the N$_{F}$ phase, and 7N/DIO coming from the SmZA$_{F}$ phase, as this condition strongly affects the textural morphology of the SmA$_{F}$ as it grows in.

For the small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) experiments, the mixtures were filled into 1-mm-diameter, thin-wall capillaries and the director $n$ (yellow arrow in Fig. 2A) was aligned by an external magnetic field $B$ (red arrow). The SAXS and WAXS were nonresonant, with diffraction images of the samples obtained in transmission on the Soft Matter Interfaces (SMI) beamline (12-ID) at National Synchrotron Light Source (NSLS) II, a microbeam with an energy of 16.1 keV and a beam size of 2 μm × 25 μm. The magnetic field produced general alignment in the capillary, but the SmZA$_{F}$ and SmA$_{F}$ textures were somewhat polydomain, with an ~10° mosaic distribution of azimuthal orientations of $n$. The $z$ axis in the X-ray plots is taken to be along the director in the domain filling the illuminated volume.

2N/DIO. Typical SAXS and WAXS images obtained on cooling the 50:50% 2N/DIO mixture from the N$_{F}$ to the SmA$_{F}$ phase are shown in Fig. 2A. In the N$_{F}$ phase at $T = 57.9^\circ$C, we observe a nematic-like, diffuse scattering arc peaked in azimuthal orientation with scattering vector $q$ along $n$, coming from the head-to-tail pair correlation of the molecules along $n$. Line scans of the scattering intensity through these peaks are shown in Fig. 2B. As seen in the Inset of Fig. 2B, the SmA$_{F}$ phase is heralded by the appearance of a new, resolution-limited peak along $q_{||}$, first showing up at $T \sim 56^\circ$C, at $q_{||}/A_{F} \sim 0.267\AA^{-1}$, a wavevector very close to the diffuse nematic peak at $q_{||} \sim 0.271\AA^{-1}$. The Inset in Fig. 2A shows a single-domain Bragg spot on the $q_{||}/A_{F}$ of 0.267 Å$^{-1}$ ring. This behavior indicates a first-order phase transition from the N$_{F}$ to the SmA$_{F}$, in accord with our polarized light microscope observations. The corresponding layer spacing is $d_{M} = 23.5\AA$, comparable to the concentration-weighted average molecular length of DIO (23.2 Å) and 2N (23.4 Å). The absence in the SAXS images of half-order peaks at $q_{||}/A_{F} < 0.245\AA^{-1}$ coming from head-to-tail pair correlations of the molecules along $n$ indicates that there is no tendency to form bilayers. In the 2N/DIO mixture, the scattering pattern rotates in the SmA$_{F}$ phase due to dynamical textural rearrangements in the capillary with changing temperature (16). The scattering arc becomes wider in the SmA$_{F}$ as the effectiveness of the magnetic field alignment is reduced on cooling.

Finally, the equatorial Bragg spots at $q_{\perp} = q_{\perp}/A_{F}$ coming from the density modulation due to the smectic layering of the SmZA$_{F}$, which are observed in both the 2N/DIO and 7N/DIO mixtures, are shown in Fig. 4. These peaks are not visible in Figs. 2A or 3A because they are relatively weak.

Polarized optical transmission microscopy enables direct visualization of the director field, $n(r)$, and, apart from its sign, of $P(r)$. These observations provide key evidence for the macroscopic ferroelectric ordering, uniaxial optical textures, and fluid layer structure of the SmA$_{F}$ phase of the 2N/DIO and 7N/DIO mixtures. In these cells, $z$ is the alignment layer buffer direction, $x$ is the coordinate normal to the plates, and the director field $n(r)$ is parallel to the plates but may or may not be along the buffer.

7N/DIO. The 50:50% 7N/DIO mixture was studied in a $d = 3.5 \mu m$ cell with antiparallel surface rubbing (an antipolar cell) with two indium tin oxide (ITO) electrodes on one surface for applying an in-plane field across a 1-mm gap. In the N phase, the LC formed a uniformly aligned monodomain with $n$ along the buffing direction, as previously observed in the nematic phase of DIO (16). In the 7N/DIO mixture with no field applied, there is little change in sample appearance with temperature, the nematic texture being maintained upon cooling into the SmZA$_{F}$ and SmA$_{F}$ phases, as seen in Fig. 3. 1 and 2. At the SmZA$_{F}$ to SmA$_{F}$ transition, the SmZA$_{F}$ layers parallel to $n$ disappear while new SmA$_{F}$ layers, normal to $n$, form. The birefringence color is a uniform blue-green everywhere in the cell and changes only slightly during the N → SmZA$_{F}$ → SmA$_{F}$ cooling sequence, providing evidence that the phase is uniaxial or only weakly biaxial and that the optical anisotropy is nearly the same in all three phases. The uniaxiality of the N phase and the weak biaxiality of the SmZA$_{F}$ have been demonstrated previously (16).

The SmZA$_{F}$ layers adopt bookshelf geometry, with the smectic layers normal to the plates and with Rapini–Papoular type anchoring of the molecules, aligning $n$ along the buffing direction $z$ and the SmZA$_{F}$ layer normal along $y$. Buffed layers for
The application of an in-plane electric field induces rotation of domain pattern (Fig. 3), typically from nanoscale to the microscale. In the absence of applied fields, SmA phases are in a surface-induced, 50:50 wt% 2N/DIO mixture in a SmAF phase is achieved by a coarsening process in which layers with the same sign of polarization extend along the buffer direction, producing only subtle changes in the textures in the absence of applied field (compare Figs. 3 C, I, and 2), with n, z, and P all colinear. However, it can be visualized by application of an in-plane electric field normal to n. This induces rotation of P in opposite directions in domains with opposite polarization, facilitating and inducing the coarsening of the domain pattern (Fig. 3 C, 3–6). This electric field response becomes increasingly dramatic as the stripes coarsen from the nanoscale to the microscale.

After extended application of weak electric fields, the SmAF cell anneals, in the absence of further applied field, into long, rectangular bookshelf domains with uniform birefringence and excellent extinction typical of weakly oriented SmA textures, as shown in Fig. 3 D, I and 2. Sufficiently large transverse direct current fields can completely reorient the SmAF layers so that P and n become aligned along E, normal to the buffing direction (Fig. 3 D, 5). In the Nf phase, this kind of global, field-induced reorientation is essentially thresholdless, with the polarization reversing readily on applied field reversal, but in the SmAf phase, there is a distinct threshold for switching and hysteresis in the response, manifest in the polarization data of SI Appendix, Fig. S1. This behavior can be understood by considering that field-induced reorientation of a spatially uniform SmA can only be accommodated by the generation of a population of gliding edge-dislocations, an inherently nonlinear process. The effect of this threshold is immediately apparent in the polarization data of SI Appendix, Fig. S1. This behavior can be understood by considering that field-induced reorientation of a spatially uniform SmA can only be accommodated by the generation of a population of gliding edge-dislocations, an inherently nonlinear process. The effect of this threshold is immediately apparent in the polarization data of SI Appendix, Fig. S1. This behavior can be understood by considering that field-induced reorientation of a spatially uniform SmA can only be accommodated by the generation of a population of gliding edge-dislocations, an inherently nonlinear process. The effect of this threshold is immediately apparent in the polarization data of SI Appendix, Fig. S1.
phase, in contrast, this response becomes subthreshold and is eliminated from these peripheral areas, with electro-optic effects confined to the designated active areas of the cell between the electrodes, where the field is strongest, as shown in Fig. 3 D, 3–5. The field on the LC is reduced adjacent to bubbles in the electrode gap in Fig. 3 C, 3–6, due to their higher electrical impedance.

### 2N/DIO

The 50:50% 2N/DIO mixture was studied in an antipolar $d = 3.5 \mu$m cell with antiparallel surface rubbing and in a sypnolar $d = 5 \mu$m cell (with parallel surface buffing). In the antipolar cell, the surface anchoring imposes a twist structure in the Ni phase in which the director/polarization field $n(r)$, $P(r)$ rotates by $\pi$ through the thickness of the cell (11). The twisted Ni phase state appears from pinkish to bluish in Fig. 2C, which shows the cell being cooled through the first-order Ni to SmAf transition, with blue-green SmAf domains growing in the upper part of the field of view. The observation that the SmAf domains can be rotated to extinction between crossed polarizers indicates that the director twist has been expelled such that, at a point in the SmAf area, the director $n(x,y)$ has a local in-plane $(x,z)$ orientation that is the same for all $x$. The uniformity of the birefringence color indicates that the phase has a principal optic axis parallel to the plates and that the phase is uniaxial, not biaxial. The growing SmAf domains are not strongly orientationally aligned by the cell surfaces initially, most likely because of the ambivalence of these now polar domains toward the antipolar surfaces. The results of application of a weak probe electric field normal to the director are shown in Fig. 5 A–C, confirming that each domain is internally homogeneously polar (black/white arrows) with orientation along the local director, some pointing up and some pointing down. The expulsion of bend and twist of $n(r)$ by the SmAf layering, and expulsion of splay of $n(r)$ in order to eliminate polarization charge, results in steady-state textures of uniformly oriented SmAf blocks, as shown in Fig. 2D, in which there are distinct domain boundaries running either parallel or perpendicular to $n$. The boundaries parallel to $n$ (approximately vertical in these images) are polarization-reversal walls like those found in the Ni phase (7), while those perpendicular to $n$ are either melted grain boundaries of the type commonly found in SmAf phases not completely aligned by weak buffing (31) or are polarization-stabilized kinks (PSKs) (32), as sketched in the Inset of Fig. 2E. Changes in the sign of $P(r)$ across the horizontal boundaries would generate maximal space charge and are thus avoided, with jumps in the orientation of $P(r)$ at these locations being limited to 10° or less. In general, there is a tendency to form long SmAf domains of uniform polarization extended along the director, as seen in Figs. 2D and 3D. The
dependent of \( T \) image of the scattered intensity, gamut in ranged, end-to-end molecular correlations. The SmZA peak locations, at the 7N/DIO mixture is in the SmZA phase, as evidenced by the scattering along \( q \). The director is aligned in the nematic phase by a magnetic field, \( B \), but rearrangements of the sample in the capillary during cooling lead to some inhomogeneity of the SmZA and SmAF layer orientation. (A) At \( T = 36 ^\circ C \), the 7N/DIO mixture is in the SmZA phase, as evidenced by the scattering along \( q \). The diffuse peaks along \( q \), parallel to the director, come from short-ranged, end-to-end molecular correlations. The SmZA peak locations, at \( q_{ij} = q \), correspond to a layer spacing of \( d_{ij} = 60 \AA \), essentially independent of \( T \). (B) Cooling to \( T = 31 ^\circ C \) initiates a weakly first-order phase transition to the SmAf, with sharp scattering appearing simultaneously from both the SmZA and SmAF layers. The SmZA peaks at this temperature appear as extended arcs. The SmZA scattering disappears below \( T = 0.5 ^\circ C \) below the onset of the SmZA-SmAF transition, i.e., there is a narrow range of \( T \) where both the SmZA and SmAF peaks are present, which we attribute to two-phase coexistence at a first-order transition. (C) Diffraction from the 2N/DIO mixture at \( T = 71 ^\circ C \), in the middle of the SmZA phase region. (D) Radial scans of the scattered intensity along \( q \), normal to the director, obtained by azimuthally averaging \( I(q) \) over the range of \( q \) that includes the SmZA peaks. The low-temperature scan of \( B \) exhibits, in addition to the SmZA peaks, scattering at \( q_{ij} = 0.245 \AA^{-1} \) from a few SmAF domains. While dwarfing the SmZA peaks, this latter intensity is orders of magnitude smaller than the main SmAF scattering along \( q \).

internal variation of orientation within the blocks is generally only a few degrees and tends to be bend of the director field, which must be mediated by edge-dislocations in the SmAF layering system.

More detailed structures of the transition regime that mediates the growth of the uniform SmAF domains into the twisted region are shown in Fig. 5 D-F. Here, remnant diamond-shaped \( N_F \) twist domains connect to surrounding uniform SmAF domains by forming PSK domain boundaries with the polarization directions in the sample midplane indicated in Fig. 5E. Similar structures constitute the zigzag SmAF-NF boundary lines in Fig. 5E.

If the SmAF is heated into the \( N_F \) phase, the removal of the layering constraints enables the polarization-reversal walls to restructure into nematic splay-bend walls (7) extended along the director, separated by areas of uniform polarization, as seen in Fig. 2 D, 2 and 3. The horizontal melted grain boundaries disappear in the absence of layering, while the horizontal PSK lines can persist into the \( N_F \) but then also melt away, leaving only the splay-bend walls (bright lines in Fig. 2 D, 2 and 3).

Because of the antiparallel boundary conditions, the initially uniform \( N_F \) states are only metastable and the inherently twisted cores of the splay-bend walls act as nucleation sites for the formation of lower-energy, twisted domains, which eventually spread to cover the entire area (Fig. 2 D, 5).

In the synpolar cell, the surface treatment stabilizes monodomains in which \( \mathbf{n} \) is homogeneously aligned along the buffing direction. The texture and birefringence of these monodomains barely change on cooling through the \( N_F \) phase, exhibiting excellent extinction between crossed polarizers in the \( N_F \) and SmAF phases except near air bubbles, as seen in Fig. 5E. The first image shows how the uniform background \( N_F \) director field favored by the cell surfaces is distorted to accommodate the nonuniform \( \mathbf{n}(r) \) orientation imposed by the boundary conditions at the edges of the bubble, where the \( \mathbf{n}(r) \) field is tangential, a configuration that requires only bend of the director and minimizes the amount of space-charge deposited at the LC/air interface. On the sides of the bubble, the director field distortion relaxes continuously with distance, with the director field eventually becoming indistinguishable from the surrounding uniform state. At the top and bottom of
the bubble, however, the 90° angular mismatch of the circumferential $\mathbf{P}(\mathbf{r})$ and the uniform background is accommodated by a “fracture” of $\mathbf{P}(\mathbf{r})$ in the form of a PSK (32), sketched in the Inset. The PSK has a minimum-energy discontinuity in $\mathbf{P}(\mathbf{r})$, with an internal structure determined by the balance of Frank elastic and electrostatic interactions, the latter manifested as an attraction between sheets of polarization charge of opposite sign (red and green in the Inset), which stabilizes the wall. The kink orientation locally bisects the angle between the incoming and outgoing $\mathbf{P}(\mathbf{r})$ directions, leading to a globally parabolic boundary between the regions with uniform and circular-bent director fields having minimal bulk polarization charge. Such two-dimensional parabolic textures, induced by the suppression of director splay, are the structural analogs of parabolic focal conics in smectics, which are induced by the suppression of director bend (33). These parabolic defects are readily observed in NF cells, where $\mathbf{P}(\mathbf{r})$ is parallel to the bounding plates, its typically preferred orientation.

At the $\text{N}_{\text{F}}$-$\text{SmA}_{\text{F}}$ transition, the areas of uniform director orientation expand, a result of the appearance of the SmA-like layering. In the absence of edge and screw dislocations, smectics expel both bend and twist of $\mathbf{n}(\mathbf{r})$, allowing, in inhomogeneously aligned nonpolar SmA, layering defects only in the form of focal conic domains, as these require only splay of $\mathbf{n}(\mathbf{r})$. However, in the polar $\text{SmA}_{\text{F}}$ phase, splay is also suppressed because of the associated polarization charge, leading to a strong tendency to form domains of uniform $\mathbf{n}(\mathbf{r})$. As the smectic layers form on cooling, the bent-director region near the bubble, in which there is both bend and twist of $\mathbf{n}(\mathbf{r})$, is therefore reduced in size, as shown in the second image of Fig. 2E.

In the remaining region near the bubble, where there is bend and twist of the director, the induced splay and twist of the smectic layering is accommodated by layer edge and screw dislocations, neither of which generates polarization space charge.

The observed transitions to the $\text{SmA}_{\text{F}}$ phase, whether $\text{N}_{\text{F}}$ to $\text{SmA}_{\text{F}}$ or $\text{SmZ}_{\text{A}}$ to $\text{SmA}_{\text{F}}$, are first order but maintain uniform planar director orientation in cells having parallel polar anchoring (parallel, unidirectional surface buffing). The $\text{SmZ}_{\text{A}}$ to $\text{SmA}_{\text{F}}$ transition in such cells is particularly subtle, with little change observed in birefringence or texture through the transition.

**Polarization Dynamics and Field-Induced Phase Transitions.** The polarization was measured in $d = 17 \mu\text{m}$, bare-ITO sandwich cells with planar alignment of $\mathbf{n}$ and bookshelf layering of the smectics at zero field, using low-frequency (8 Hz) triangle waves. The electrical response of the 2N/DIO and 7N/DIO mixtures as a function of temperature is summarized in *SI Appendix*, Fig. S1. At the beginning of the current–voltage cycle, shown in *SI Appendix*, Fig. S1A for the 2N mixture, the applied voltage is large and negative ($V(t) \sim -30 \text{ V}$), at which time any ions have been pulled to the cell surfaces so there is no ion current. In the $\text{N}$ phase ($T > 84^\circ\text{C}$), the current shows a bump following the sign change of $V(t)$, which we attribute to ions. In the $\text{SmZ}_{\text{A}}$ phase ($84^\circ\text{C} > T > 68^\circ\text{C}$), the polarization current is combined with the ion current following each sign change of $V(t)$, so the polarization $P(T)$ is obtained by doubling the $I(t)$ area left of the center line, where the ion current, taken as that at the lowest temperature in the $\text{N}$ phase, is small and subtracted out. The $\text{SmZ}_{\text{A}}$ exhibits LC repolarization peaks that appear when the applied negative voltage is decreasing, growing in area and with their peak center voltages $V_{\text{p}}$ moving toward zero on cooling, behavior very similar to that of neat DIO (see Fig. 5 in ref. (7)). This is typical antiferroelectric behavior, the peaks marking the return at finite voltage of the field-induced ferroelectric state to the antiferroelectric ground state. In the $\text{N}_{\text{F}}$ phase, the Goldstone-mode mediated reorientation and reversal of $\mathbf{P}$ produces a current peak at the zero crossing of $V(t)$ (cyan scans), followed by an ion peak at some later time. $P(T)$, taken as the area of the big peak, is found to grow more slowly on cooling in the $\text{N}_{\text{F}}$ than that of neat DIO or RM734 (7) or their mixtures (9), possibly a result of the increasing short-range $\text{SmA}_{\text{F}}$ order. At the transition to the $\text{SmA}_{\text{F}}$ phase, $P$ jumps up to a $T$-independent value and the ion current disappears altogether due to screening of the field in the LC due to polarization charge. Polarization reversal occurs after the zero crossing, at a finite voltage corresponding to the coercive field $E_c$ plotted as solid symbols in *SI Appendix*, Fig. S1B and shown schematically in the adjoining hysteresis loop.

*SI Appendix*, Fig. S1C and D show the results for the 7N/DIO mixture, where the Goldstone feature of the $\text{N}_{\text{F}}$ is absent, heralding the direct $\text{SmZ}_{\text{A}}$ to $\text{SmA}_{\text{F}}$ transition. The $\text{N}$ phase again exhibits a large current peak following the sign change of $V(t)$, so $P(T)$ in the $\text{SmZ}_{\text{A}}$ is again obtained by doubling the $I(t)$ area left of the center line, with the $\text{N}$ phase current as a background. As in *SI Appendix*, Fig. S1A and B, the ion current disappears in the $\text{SmA}_{\text{F}}$ phase and the integration is carried out over the whole $V(t)$ range (Fig. 6).

**Discussion.** These observations, and the recent report that replacing only a single H atom on DIO with an F atom can produce a homolog that exhibits the $\text{SmA}_{\text{F}}$ phase as a single molecular component.
and the equilibrium antiferroelectric state. In the NF phase, (cyan curves)
cooling. This is typical antiferroelectric behavior, the peaks marking the
curves) following the sign change of the function of temperature with 8 Hz triangle-wave voltage (white trace)
reorientation appears on cooling run. In the N phase, the ion current disappears
an N phase (red construction). (b) 7N/DIO current response – The plots show the current response during an N \( \rightarrow \) SmZA cooling run. In the SmZA phase (84 °C > T > 68 °C, green curves), two polarization peaks are seen during this half-cycle of the applied voltage, growing in area and occurring at smaller voltage on cooling.

At this transition, the polarization jumps to saturation and Bragg peaks appear at \( q || \) ∼ 2π/ξ ∼ 0.25 Å\(^{-1}\). This peak appears in RM734 and DIO (SI Appendix, Figs. S2–S4 (9)), and in the 2N/DIO and 7N/DIO mixtures (Figs. 2–4). Its line shape can be used to estimate molecular positional correlation lengths, \( \xi || (T) \) and \( \xi \perp (T) \) (SI Appendix, Sec. S3). In the mixtures, at temperatures well above the transition to the SmZA phase (Figs. 3B and 4C), we find \( \xi || \sim 30 \) Å and \( \xi \perp \sim 4 \) Å, indicating linear, end-to-end, chain-like associations of approximately two to three molecules, without much side-by-side interaction, and only a weak temperature dependence.

In the RM734/DIO mixtures, the saturation \( P \) is achieved in the NF under this circumstance. In the 2N and 7N mixtures, however, the corresponding polarization values are well below saturation but grow continuously with decreasing \( T \), as shown in SI Appendix, Fig. S1. Additionally, as the mixtures are cooled into the range ∼10 °C above the SmAz transition, the diffuse scattering peak substantially narrows in \( q \) and the correlation lengths exhibit a second-order type, pretransitional divergence, increasing in 2N/DIO to \( \xi || \sim 200 \) Å and \( \xi \perp \sim 14 \) Å at \( T = 55 °C \), where the first-order transition to the SmAz takes place for this mixture.

At this transition, the polarization jumps to saturation and Bragg peaks appear at \( q || = q ||,AF \) at the spacing of the diffuse peak in the X-ray structure factor, and with a resolution-limited width (\( \xi ||, \xi \perp \sim 700 \) Å). This indicates that head-to-tail molecular association, which grows with increasing \( P \) in the Nf and SmZ\( A \) phases, is cooperatively coupled to, and mutually promotes, the SmAz layering.

The plots show the current response during an N \( \rightarrow \) SmAz cooling run, exhibiting the same overall features as the 2N/DIO mixture, except for the notable absence of the current peak at the zero-crossing of \( V(t) \), indicative of an Nf phase. The 7N mixture gives the largest ion currents among the mixtures and Dio, but in the 7N nematic this may be some kind of antiferroelectric pretransitional effect of the nematic, since the current peak observed at positive voltage evolves into the SmAz polarization peak with decreasing \( T \). As with the 2N/DIO mixture the ion peak is not observed in the ferroelectric phase. (c) 7N/DIO polarization – Polarization values \( P(T) \) (open circles) were obtained by integrating the current as before, increasing substantially and monotonically in the SmAz, and saturating in the SmAf.
These X-ray features, the observed \( J(\pi) \) values, and the atomistic simulations of RM734 indicate that the appearance of the SmA\(_E\) phase is a cooperative coupling of dynamic head-to-tail, polar, chain-like correlations with SmA\(_1\) layering correlations. This sort of ordering may be compared with that of the antiferroelectric uniaxial polar smectics of rod-shaped molecules noted above (19–21), in which the end-to-end association preference is antiferroelectric (with head-to-head/tail-to-tail chain correlations) rather than ferroelectric. When this kind of association is dominant, the resulting phases are antiferroelectric and a rich palette of nematic, smectic, and re-entrant phases emerges, controlled by the preferred relative positions of neighboring chains along the director. For example, side-by-side association of ends irrespective of whether they are heads or tails results in the monolayer SmA\(_1\) phase, a nonpolar dielectric with a layer spacing close to the molecular length; condensation of paired heads in planes gives the antiferroelectric bilayer ordering of the SmA\(_2\) phase; and alternation of domains of paired heads and tails in a plane gives the modulated SmA\(_4\) phase. Nematic phases appear as a result of frustration between competing smectics of different layer periodicity.

It appears that, with the coming of the SmZ\(_A\) and SmA\(_E\) phases, a similar story may be emerging in the N\(_F\) realm, this one based on polar head-to-tail correlations. The SmA\(_E\) is apparently a monolayer smectic, a ferroelectric SmA\(_1\) in the terminology of the earlier polar smectic literature, with some degree of side-by-side ordering of chains having parallel polarizations. In this regard, it is worth recalling that the antiferroelectric polar smectic phases and the transitions between them have been modeled with some success by Berker and coworkers, who formulated hexagonal lattice (frustrated spin-gas) models, comprising finite-length columns of molecules with intra-column, end-to-end interactions and intercolumn, side-by-side interactions (35–38). The simplest useful versions of these models are lattices of three distinct, finite-length column configurations, which capture the inherent frustration of hexagonally packing antiferroelectric columns interacting side by side. Such models enable exact statistical mechanics to be carried out, revealing theoretically the rich polymorphism of the antiferroelectric smectic polar phases and describing well multiply re-entrant phase sequences, including the N, SmA\(_E\), reentrant N, and SmA\(_1\) phases. While the focus of this earlier work has been on antiferroelectricity, this approach has recently been applied by Madhusudhana (39) to N\(_F\) ordering, showing that macroscopic ferroelectricity is achievable with model dipolar rods with similar dimensions and molecular-charge distribution to the molecules of the N\(_F\) realm. The application of such models to the SmA\(_E\) phase should be particularly revealing since, being a monolayer SmA\(_1\), the SmA\(_E\) seems to require the ferroelectric ordering of side-by-side molecules. An effective approach to pursuing such modeling will be to use atomistic simulation to evaluate the actual forces between side-by-side chains.

**Materials and Methods**

The mixtures were studied using standard LC phase analysis techniques described previously (7, 10, 16), including polarized transmission optical microscopy observation of LC textures and their response to electric field, X-ray scattering (SAX and WAXS), and techniques for measuring polarization and determining electro-optic response.

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**Materials.** DIO, shown in Fig. 1 and first reported in ref. (6), was synthesized for these experiments as described in ref. (9). Synthesis of AUUQL2N and AUUQL3N, also shown in Fig. 1, followed that of AUUQL3N, described in ref. (40). The phase transition temperatures obtained upon slow cooling (∼1 °C/min) are shown in Fig. 1. Optical microscopy as in Figs. 2 and 3, polarization measurements as in SI Appendix, Fig. S1, and changes in the X-ray scattering peak intensity as in Figs. 24 and 34 were used to locate the transitions. The 2N/DIO and 7N/DIO mixtures can be cooled at ∼1 °C/min to 25 °C, where they exhibit the SmA\(_E\) phase, which is monotropic with respect to crystallization. Crystallization proceeds very slowly, however, with samples remaining for days to weeks in the SmA\(_E\) phase. Upon heating, the fully crystallized 2N/DIO and 7N/DIO mixtures melt over a few °C range, at around 85 °C, into the N phase.

**X-Ray Scattering.** For the SAX and WAXS experiments, the LC samples were filled into 1-mm-diameter, thin-wall capillaries. The director \( \mathbf{n} \) was aligned with an external magnetic field normal to the beam. Diffraction data presented here were obtained on the SM1 beamline at NSLS II with a photon energy of 16 keV (wavelength = 0.775 Å). At this wavelength, the desired range of scattering vectors \( q < 0.5 \AA^{-1} \) encompasses a small range of scattering angles \( (0 < \theta < 30°) \), so that the Ewald sphere can be approximated as an Ewald plane. The Ewald sphere can be approximated as an Ewald plane. The Ewald sphere can be approximated as an Ewald plane.

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