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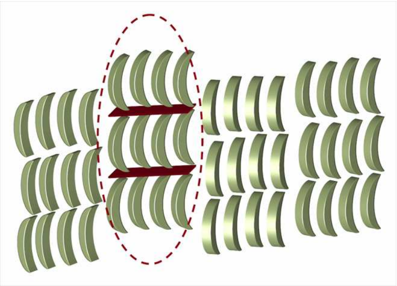
Cybotaxis, the molecular clustering observed in bent-core nematics, governs the unique properties of this new class of anisotropic fluids.



The cybotactic nematic phase of bent-core mesogens:
State of the art and future developments

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Abstract

The molecular clustering observed in the fluid nematic phase of nonlinear liquid crystal molecules underlies exaggerated field effects that portend unique technological advances in next-generation liquid crystal displays. However, the detailed nature of the molecular organization within the clusters and the temporal and spatial persistence of that organization remain unclear. Herein we review the evolution of structural studies of this unique nematic phase. The mounting experimental evidence points to a converging picture of the microscopic nature of this relatively new class of liquid crystals.

Nonlinear bent-core mesogens that exhibit the nematic (N) phase were discovered in 2000 and since then they have been the subject of an intense experimental and theoretical investigation due to both their unique properties and potential for fast switching displays.[1] Additionally, bent-core nematics (BCNs), such as those shown in Chart 1, have been regarded as promising candidates in the search for the elusive biaxial nematic (N_b)[2,3] and polar ferroelectric nematic (N_f)[4] phases. It is now clear that the origin of BCNs' unconventional properties resides in the nature of the short-range intermolecular correlations characterizing their N phase. This phase and the interpretation of the associated *four-spot* small angle X-ray scattering (SAXS) pattern (remarkably different from the *two-spot* SAXS pattern exhibited by linear calamitic nematics) are issues that have attracted great interest and generated a lively debate within the liquid crystal (LC) community. Initially, the four-spot SAXS pattern of an aligned BCN was interpreted as the signature of biaxial orientational order: the four small angle diffuse spots were thought to arise from the form factor of a nonlinear mesogen in conjunction with a biaxial nematic structure factor.[2] Subsequently, the peculiar four-spot pattern has been interpreted as evidence of short-range, tilted—smectic (Sm) C-like—intermolecular correlations similar to the pretransitional SmC order observed in conventional calamitic nematics.[4-9] Although the scientific debate about this topic is ongoing, there is currently a general consensus emerging that the unconventional behavior of BCNs is due to the *cybotactic* nature of the N phase.

The adjective *cybotactic* (from the Greek noun *cybotaxis*, meaning *space arrangement*) was originally proposed by Stewart and Morrow[10] in 1927 to differentiate the short-range structure apparent in the scattering of simple liquids from the long-range structure in the crystalline state. By analogy, *cybotactic nematic* was introduced into LC terminology in 1970 by Adrian de Vries[11] to differentiate the pretransitional, short-range, incipient Sm supramolecular structure fluctuations in calamitic nematics from the long-range, stratified structure of the Sm phase itself. In recent years, interest in cybotactic order has been rekindled in connection with evolving studies of the N phase of bent-core molecules. Herein, after an overview of the main steps that underlie the emergence of the cybotactic picture of BCNs, we will discuss the state of the art and future developments of this subject.

The first reference to cybotactic order in BCNs was reported in 2002 for a 1,2,4-oxadiazole derivative, namely BCN **1** in Chart 1.[12] It was based on the distinctive four-spot splitting of the diffuse SAXS feature (Fig. 1). Similar conclusions were reached by Stojadinovic *et al.* on the basis of Dynamic Light Scattering (DLS) measurements,[13] and later by Domenici *et al.* using NMR techniques.[14] The cybotactic model of the N phase assumes the existence of short-range Sm-like ordering in the form of nanometer-sized clusters (cybotactic groups) exhibiting a layered supramolecular structure (typically skewed, i.e. SmC-like) with intrinsic biaxial orientational order (Fig. 1). Cybotactic clustering—local coalescing of molecules into layered domains—is generated by frustration of translational diffusion of the bent-shaped molecules. This forces the classical N order (liquid-like positional order and uniaxial orientational order) to develop on a length scale larger than the size of the clusters. The origin of this appears to be intimately associated with molecular shape: Virtually all linear calamitic mesogens do not have cylindrical symmetry even when one generates a *molecular envelope* by pre-averaging over internal molecular degrees of freedom (e.g., dihedral angles). Consequently nearest neighbor packing considerations in the translationally disordered N phase dictate local orientational correlations in the plane transverse to the N director **n**. This prompted the suggestion that all nematics are locally biaxial.[15] The envelope of nonlinear bent-core mesogens exaggerates such transverse correlations. And, when the envelope's shape anisotropy is very extreme, such transverse orientational correlations in a translationally disordered nematic necessarily involve multiple molecules along **n**. The number of molecules impacted by a given molecule's azimuthal orientation—the extent of transverse correlations—is reduced if the nonlinear molecules coalesce locally into strata, i.e., form cybotactic clusters. In this way one can begin to understand the implications of changing mesogen shape from linear to bent: Nonlinearity merely amplifies the role of transverse orientational correlations, and that, in turn, precipitates the formation of new kinds of N supramolecular organization in BCNs.

Unlike calamitic LCs, where cybotactic order is primarily manifested as a pretransition effect restricted to the vicinity of an underlying Sm phase, cybotactic order in BCNs persists over the entire N range up to the isotropic (I) phase, and it does not exhibit critical behavior on approaching the N-SmC phase transition.[4,6-9] Fig. 2 shows the temperature evolution of the SAXS patterns of two representative BCNs based on the 1,3,4-oxadiazole biphenol (ODBP) moiety, namely BCNs **2a** and **2b** in Chart 1.[7] In Fig. 2a-f, the four-spot pattern is apparent at all temperatures up to the clearing point ($T_{N\text{-}I}$), consistent with a skewed, SmC-like cybotactic N phase (N_{cyboC}) extending over the entire N range. In Fig. 2g-l, the evolution from the high-temperature pattern consisting of two diffuse meridional peaks to the low-temperature four-spot pattern was interpreted as a supramolecular structural transition (at $T\text{-}\ T_{N\text{-}I} \approx -6$ °C, Fig.2i) between two different types of cybotactic N phases, namely the tilted N_{cyboC} at low temperature and, at higher temperature, the untilted N_{cyboA} (i.e. a cybotactic N phase with a *normal* layered SmA-like supramolecular structure within the clusters). The temperature dependence of the relevant structural parameters from the SAXS data—an increase of the layer d spacing with a concurrent reduction of the tilt angle β (Fig. 1), which compensate one another to make the estimated molecular length $L = d/\cos\beta$ reasonably constant over the entire N range—provided indisputable proof that the evolution of the SAXS splitting originates from a *supramolecular* structural change (i.e., results from the change of the tilt angle)[6,7] rather than from an *intramolecular* geometrical change in conjunction with a biaxial N structure factor as initially reported.[2] The temperature dependent data was a strong confirmation of the cybotactic model of BCNs.

The cybotactic model was invoked to explain the ferroelectric-like response to a switching electric field, observed for the first time in the N phase of BCN **1**.[4] Cooperative alignment of nanometer-sized biaxial and polar clusters (polar cybotactic groups) was proposed to cause the ferroelectric-like response: In the absence of an electric field **E**, the clusters' transverse polar axes are randomly oriented, so that the macroscopic polarization averages to zero. However, an external **E** field above a certain threshold is able to align the clusters' dipoles over the macroscopic sample, causing a transition to a ferroelectric state characterized by a macroscopic polarization of 10 - 100 nC cm^{-2} (depending on the temperature). Once this polar state has been established, the polarization can be reversed by changing the sign of **E**, through the cooperative rotation of the mesogens of each group about the long molecular axis.[4] Similar results were later obtained for other 1,2,4-ODBP-based BCNs, where the cybotactic model of ferroelectric-like switching was also confirmed by dielectric spectroscopy measurements.[16]

The cybotactic nature of molecular order in BCNs was originally advanced to rationalize experimental findings. Subsequently this picture was confirmed by molecular dynamics simulations,[4,17] providing a microscopic underpinning of the phenomenological theory developed by Photinos and coworkers.[18] This latter theory is based on the Landau-De Gennes expansion of the free energy in terms of three primary order parameters: the cluster biaxiality (polarity) order parameter, describing the average internal biaxial (polar) order, the macroscopic biaxiality order parameter, and the macroscopic polarity order parameter. In the absence of an external field, the model predicts the existence of four possible distinct N phases: a proper high temperature uniaxial phase, an intermediate uniaxial phase with local polar order formed by uniaxially-distributed biaxial clusters, a biaxial apolar N phase, and a biaxial polar phase. Depending on the relative values of the expansion parameters, this model can accommodate different thermotropic or field-induced phase sequences.

The nature of the short-range positional correlations underlying the cybotactic order was originally associated with the pretransitional Sm-like fluctuations observed in calamitic nematics in the vicinity of the N-SmC transition. Accordingly, theoretical models[5] assumed a structure factor $S(\mathbf{q})$ for the scattered intensity having the form of the modified Lorentzian function (Eq.(1)) derived from the classical Landau-de Gennes theory of phase transitions[19-21]

$$S(\mathrm{q}) \propto \left\{ \left[1 + \xi_{\|}^{2} \left(q_{\|} \pm q_{0\|} \right)^{2} \right]^{2} + 2\xi_{\perp}^{2} \left[1 + \xi_{\perp}^{2} \left(q_{\perp} \pm q_{0\perp} \right)^{2} \right] \left(q_{\perp}^{2} + q_{0\perp}^{2} \right) + \xi_{\perp}^{4} \left(q_{\perp}^{2} - q_{0\perp}^{2} \right) \right\}^{-1} , \qquad (1)$$

where $\xi_{||}$ and $\xi_{\perp}$ are the longitudinal (|| **n**) and transversal (⊥ **n**) positional correlations lengths and q_0 is the modulus of the wavevector corresponding to the four-spot intensity maxima. However, the anomalously large width of the temperature range exhibiting such fluctuations (the entire N range, i.e. several tens of degrees in certain BCNs),[4-9] together with the absence of observed critical behavior of the correlation lengths near the N-SmC transition,[4-7] early on called into question the assumption for $S(\mathbf{q})$. Clear evidence of cybotactic order for BCN **2c** that does not exhibit an underlying Sm phase (mesophase sequence: I – N – Crystal, see Fig. 3a) shows that cybotactic clustering in BCNs is a phenomenon unrelated to pretransitional cybotaxis.[6] Consistent with that, attempts to fit the SAXS data using the Lorentzian-modified function in Eq. (1) failed to satisfactorily reproduce the experimental data,[6] thereby reinforcing the proposal that the classical model of pretransitional fluctuations in conventional nematics does not work in descriptions of the correlation fluctuations underlying cybotaxis in BCNs. On the other hand, in the more general case of BCNs with an underlying SmC phase (mesophase sequence: I – N – SmC), SAXS investigation of the N-SmC phase transition provided further confirmation of the above conclusion. As an example, Fig. 3b shows the SAXS pattern of BCN **2a** captured in the process of incipient N-SmC phase transition. In principle, clustering as a pre-transitional effect would involve SmC-order condensation—and its critical growth from a short-range to long-range scale—developing from the embryonic SmC cybotactic clusters of the N phase. However, what is apparent in Fig. 3b is that the transition starts and evolves with both an abrupt change of the *d* spacing (as evidenced by the change of the radius of the ring through the intensity maxima) and an azimuthal intensity spreading that follows a different shape (circular vs elliptical). On this basis, the emerging picture of cybotactic order in BCNs[6,15] would be that of *dynamic*, local, positional correlations having the form of Sm fluctuations—evanescent density waves with the Sm layer either titled (N_{cyboC}) or normal (N_{cyboA}) relative to the director **n**—generated by microscopic interactions fundamentally different from those underlying the classical pretransition phenomena.[6] Nevertheless, there are more *static* interpretations of cybotactic nematics wherein the clusters persist as stable entities in the melt.

In particular, a recent SAXS study has shown that a nanostructure based on *discrete*, finite-sized Sm-like clusters of molecules (i.e., well defined SmC-like domains of finite extent) provides a more accurate description of the diffraction data from BCNs than the standard models used to describe fluctuating Sm order in calamitic nematics.[22] However, some assumptions in this model, e.g. the temperature independence of the tilt angle of the SmC layers, do not seem properly justified. This calls into questions the authors' conclusions about the capability of their analysis to *unequivocally* assign a static or dynamic nature to the cluster structure. We believe that the nature of the short-range order still remains an open question that deserves further investigation with the aid of experimental techniques able to probe the nanoscale dynamical features of the system. Whatever the inherent nature—static or dynamic—the existence of cybotactic clusters was recently reinforced by means of cryo-TEM imaging.[23] For example, the cryo-TEM images in Fig. 4 show evidence of Sm (cybotactic) clusters on length scales of 30–50 nm in the N phase of a bent-core compound.[23] It is important to note that the cluster sizes (longitudinal width, W, and transversal length, L) apparent in the TEM images are larger (up to 1 order of magnitude) than those estimated via the positional correlation lengths ($\xi_{\parallel}$ and $\xi_{\perp}$) deduced from appropriate analysis of the intensity profiles of the SAXS spots.[2,4,6,7,22,24] Part of this difference may be ascribed to the analytical models adopted to measure the extent of the short-range order. However, recent insights into the details of the SAXS pattern of the N_{cyboC} phase (in particular the spreading of the scattered intensity maxima along an elliptical trace as shown in Fig. 3b)[25] point to a significant contribution from the orientational distribution function of the cybotactic domains to the broadening of the small-angle diffuse spots. In that case the reported values of correlation lengths should be interpreted as the lower limits of cluster size, thus strengthening the agreement with the cryo-TEM observations.

Recent studies of the thermotropic phase behavior of BCNs under an applied magnetic (**H**)[26] or electric (**E**)[27] field have further confirmed the inherent nature of the N with regard to its constitutive entities, i.e. nanometer sized clusters *versus* individual molecules. Figs. 5a and 5b show the 2D temperature-field phase diagrams of **2a** in (T, H) and (T, E) space, respectively. These results show that fields of modest intensity (*H, E*), that in conventional nematics do not produce any appreciable effect on the thermodynamics of the system, strongly affect both the mesophase sequence and the transition temperatures of BCNs. In particular, an extraordinary field-induced shift of the *N–I* phase transition is found, which has neither any experimental counterpart in conventional calamitic LCs, nor can it be explained by the presently available theories of phase transitions. Conversely, these results are in close agreement with the cluster theoretical model,[18] that predicts an enhanced sensitivity of the N_{cybo} phases to an applied field. In conventional (molecular) nematics, where the applied field couples to the anisotropy of individual molecules, the field produces only a minute effect on molecular orientational ordering. By contrast, in the N_{cybo} phase of BCNs the field couples to an entire (biaxial) cluster of partially ordered molecules which, in turn, magnifies the field effects by a factor proportional to the average number of molecules per cluster,[26,27] i.e. a few hundred molecules.[6,7,22,23] Beyond its fundamental importance, the strongly enhanced field sensitivity of the N_{cybo} state of matter is important from a practical point of view: it compels one to consider field effects in BCNs within the framework of a two-dimensional temperature-field phase diagram.

Based on the results observed so far, the current challenges to researchers in this field include the following, partially interconnected issues: (*i*) an indisputable experimental proof of the existence of a *spontaneous* macroscopically biaxial N phase in BCNs; (*ii*) a deeper understanding of the real nature of the polar order underlying the ferroelectric-like switching response observed in the N_{cybo} phase of a few BCNs;[4,16] (*iii*) the possibility of extending the N_{cybo} temperature range down to room temperature to exploit cybotaxis in practical applications; and (*iv*) the exploration of the extent to which cybotactic order (and related properties) can be *translated* to yield a deeper understanding of the N phase of other systems, e.g., polymeric LCs and more complex composite ordered fluids.

Regarding the first issue (*i*), the N_b phase of BCNs, originally claimed in 2004[2,3] is still controversial and its very nature—spontaneous *vs* induced, local *vs* macroscopic—is still a widely debated issue.[28-37] In fact, whereas all of the presently available experimental results are consistent with the presence of local biaxial clusters (which can be macroscopically ordered into a N_b state under the action of an external aligning field or directional surface anchoring), none of the experimental results on thermotropic biaxial nematics seems to provide a *direct* unequivocal proof of the spontaneous formation of a macroscopic (monodomain) N_b phase. With respect to issue (ii) the ferroelectric-like switching response observed in a few asymmetric ODBP BCNs by different groups[4,16,38] is motivating a deeper investigation on the fundamental nature of this polar response via complementary techniques such as second harmonic generation (SHG).[39]

As part of an effort to access the cybotactic (potentially biaxial and/or ferroelectric) N phase at low temperatures—issue (iii)—a series of 1,3,4-ODBP BCMs was recently prepared that possess either one (**3a**, **3b**) or three (**3c**, **3d**) lateral methyl groups.[40] X-ray diffraction experiments confirmed the presence of cybotactic clusters in the N phase of all the derivatives. In particular, the derivatives with three methyl substituents showed low N onset temperatures and could be supercooled in the N phase to room temperature in a metastable, highly viscous state (Fig. 6). Especially noteworthy is the observed splitting of the wide-angle XRD feature over the entire N range; this is the first *direct* scattering evidence of local biaxial order in the N phase of a bent-core mesogen.[41] These results earmark the substituted ODBP materials as promising candidates in the search for low-temperature, thermotropic biaxial nematics.

With respect to the last issue (*iv*), recently for the first time a LC polymer made of bent-core mesogenic repeat units (**4**) has been demonstrated to exhibit cybotactic order in its N phase.[42] Similar to low molar mass BCNs, the analysis of the SAXS patterns (inset of Fig. 7) reveals a N phase made of nanometer-sized cybotactic groups containing a few hundred monomer units. The covalent polymer chain mesogenic core linkage constraints result in maximized orientational correlations among clusters that make this material of great potential in the search for the elusive N_b and N_f phases. Indeed, repolarization current measurements in the N phase hint at a ferroelectric-like switching response on application of an electric field as low as 1.0 V μm^{-1}. The corresponding macroscopic polarization (up to 0.85 $\mu C\ cm^{-2}$) is one order of magnitude larger than that of the low molar mass counterpart **1** and, since the average size of the cybotactic groups is the same, the enhanced polarization is attributed to the polymeric nature of the material, i.e. to the effects of intrachain covalent bonds that strengthen the dipolar orientational correlations among the cybotactic clusters. Once definitely confirmed by complementary techniques, the large polarization value and the relatively low switching field of this material might open new possibilities for innovative applications in polymeric ferroelectric devices. Finally, the weak tendency of this polymer to crystallize makes it possible to supercool the N_{cybo} phase down to room temperature, thus paving the way for a glassy phase in which the biaxial (and possibly polar) order is locked in at room temperature, with potential applications in ferroelectric data storage devices.

In summary, a deeper understanding of the fundamental nature of cybotaxis in BCNs is envisaged in the near future which, when coupled with the ability to manipulate nanoscale (polar) order, could open up completely new LC-based technological applications.

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Figure Captions

Charter 1. Molecular structures of mentioned BCNs.

Figure 1. Schematic drawing of the molecular arrangement within a skewed cybotactic cluster (aligned under a horizontal magnetic field **B**) together with the corresponding SAXS pattern. The four spots result from the azimuthal degeneracy of the normal to the Sm planes **k**, which generates a cone of semi-aperture β around the molecular director **n**. The expression $q_0 = 2\pi/d = 2\pi / L\cos\beta$ relates the modulus of the scattering vector, q_0, to the structural parameters (i.e. layer spacing d, molecular length L, and tilt angle β).

Figure 2. SAXS patterns of two representative BCNs recorded on cooling from the isotropic melt under a horizontal magnetic field, at different values of the reduced temperature $T - T_{N\text{-}I}$: (a-f) **2a**; (g-l) **2b**.

Figure 3. The SAXS patterns of: (a) **2c** at the $\mathrm{N_{cyboC}}$-crystal phase transition temperature; (b) **2a** at the $\mathrm{N_{cyboC}}$-SmC phase transition temperature.

Figure 4. Cryo-TEM observations on a cybotactic BCN after quenching from (a) 90 °C, (b) 80 °C, (c) 70 °C, and (d) 65 °C. Stripped domains are SmC-like clusters of molecules. Reprinted with permission from C. Zhang *et al.*, *Phys. Rev. Lett.*, **109**, 107802, 2012 (ref. 23). Copyright 2012 by the American Physical Society.[1]

Figure 5. Phase diagrams of **2a** in the two-dimensional (a) (H, T) and (b) (E, T) space (E_0 = 0.62 V μm^{-1}, ν = 500 Hz). The square symbols indicate the measured phase transition temperatures; interpolated phase boundaries are drawn as a guideline to the eye.

Figure 6. SAXS patterns of **3d** collected at different temperatures under the following experimental conditions: (a)–(b) on cooling from the isotropic melt with B = 1 T (horizontal); (c) B = 0 just at the

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end of the cooling cycle; (d) B = 0, 17 hours after the end of the cooling cycle. Pictures (b)-(d) correspond to the supercooled N_{cyboC} phase.

Figure 7. Repolarization current response in the N_{cyboC} phase of LC polymer **4**, measured at 248 °C (blue solid line) and 216 °C (red solid line) upon application of a triangular wave voltage (f = 1 Hz, black dotted line). The two arrows indicate the current peaks associated with the polarization switching. In the lower inset, the peaks disappear when the measurement is performed in the isotropic phase (293 °C, green solid line). In the upper left corner, a typical SAXS pattern of the LC polymer in its N phase.

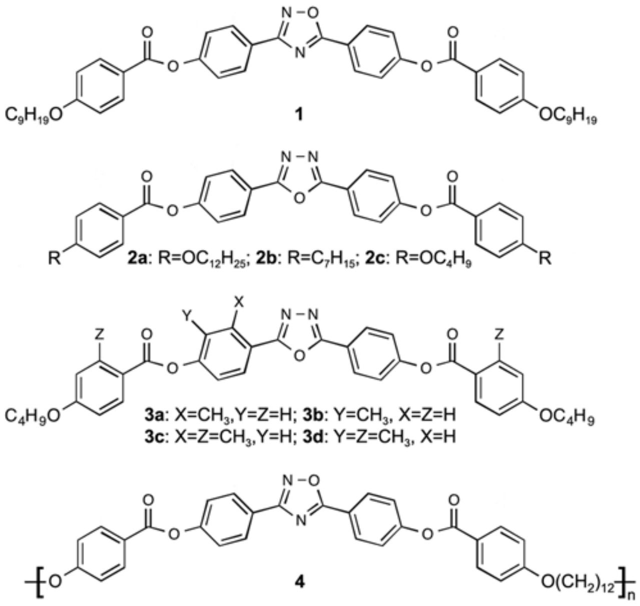

C9H19O
OC9H19
1
2a: R=OC12H25; 2b: R=C7H15; 2c: R=OC4H9
X
Y
Z
C4H9O
OC4H9
3a: X=CH3,Y=Z=H; 3b: Y=CH3, X=Z=H
3c: X=Z=CH3,Y=H; 3d: Y=Z=CH3, X=H
4
O(CH2)12
n

Chart 1

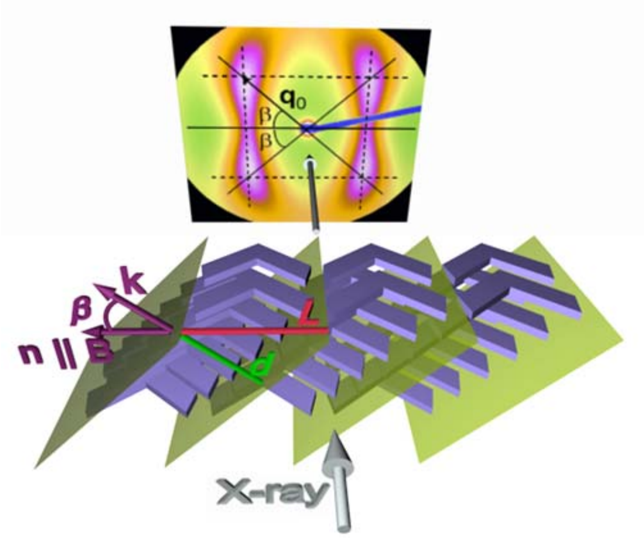


Figure 1

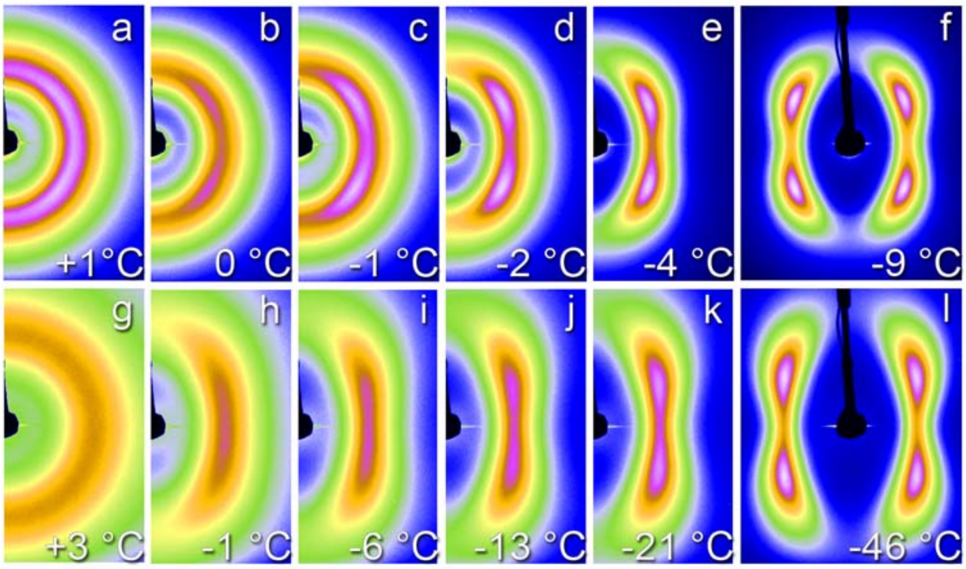


Figure 2

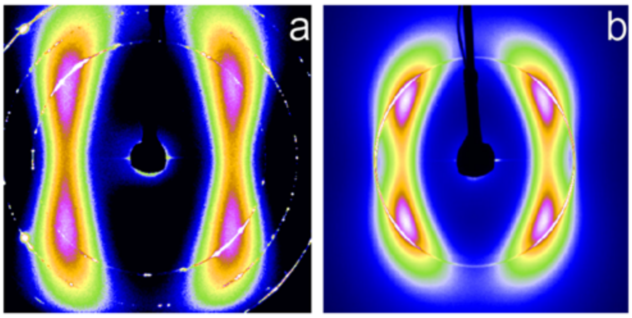


Figure 3

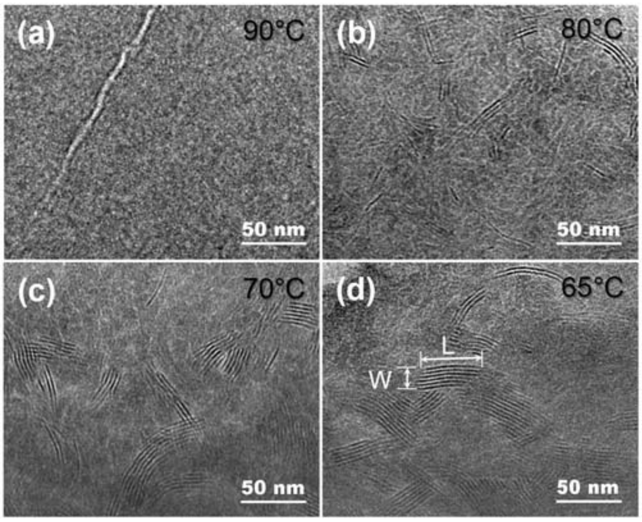


Figure 4

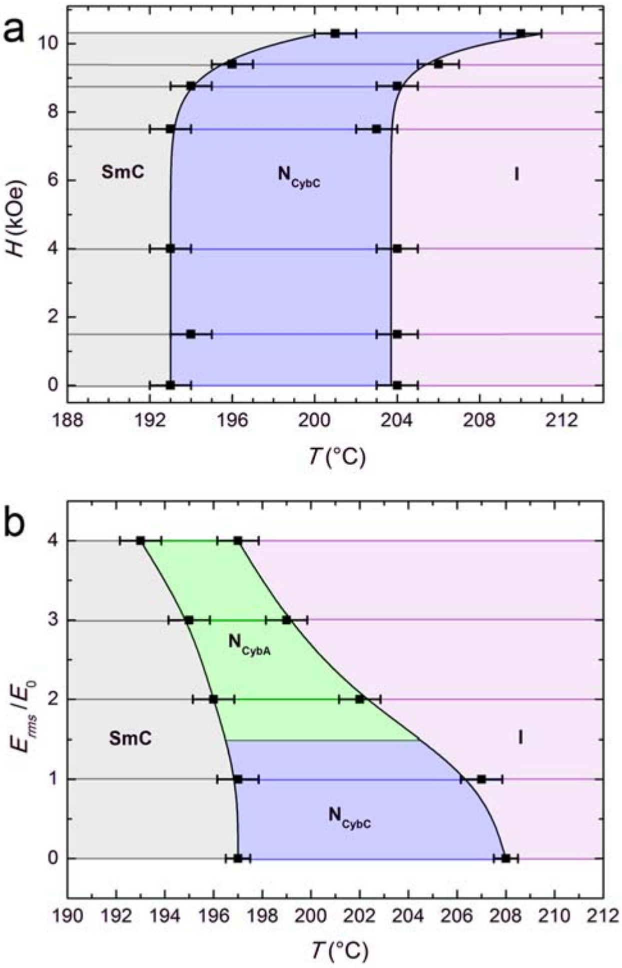

a
SmC
N_{CybC}
I
H (kOe)
0
2
4
6
8
10
188
192
196
200
204
208
212
T (°C)
b
SmC
N_{CybA}
N_{CybC}
I
E_{rms}/E_0
0
1
2
3
4
190
192
194
196
198
200
202
204
206
208
210
212
T (°C)

Figure 5

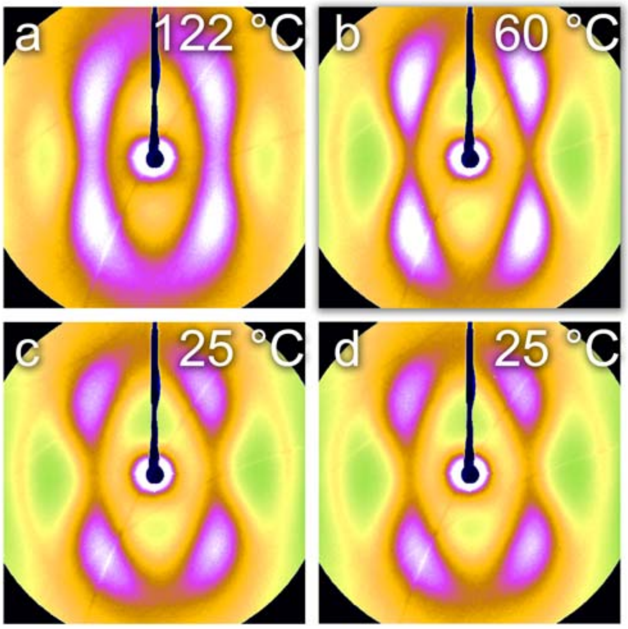
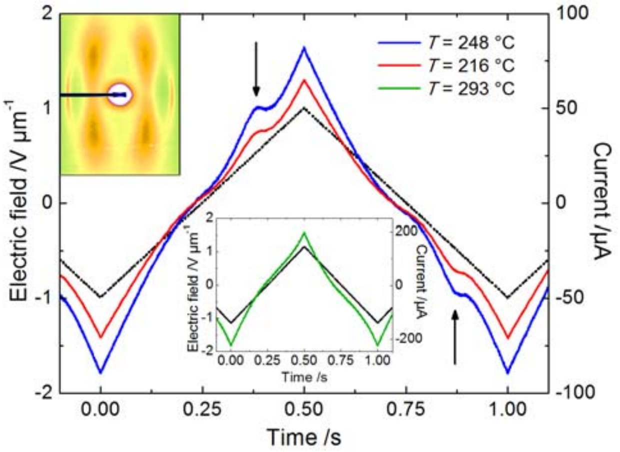


Figure 6



2
1
0
-1
-2
Electric field /V µm^{-1}
100
50
0
-50
-100
Current /µA
0.00
0.25
0.50
0.75
1.00
Time /s
T = 248 °C
T = 216 °C
T = 293 °C
2
1
0
-1
-2
Electric field /V µm^{-1}
200
0
-200
Current /µA
0.00
0.25
0.50
0.75
1.00
Time /s

Figure 7