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Electro-Optic Response of the Anticlinic, Antiferroelectric Liquid Crystal Phase of a Biaxial Bent-Core Molecule with Tilt Angle near 45º

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Abstract

The rapid electro-optic response of polar smectic liquid crystal phases has led to their application in a variety of electro-optic devices. We describe the unusual electro-optic response of a biaxial bent-core molecule that exhibits an anticlinic, antiferroelectric smectic phase (SmC_AP_A) with a molecular tilt angle close to 45°. In the ground state, the sample shows very low birefringence. A weak applied electric field distorts the antiferroelectric ground state, inducing a small azimuthal reorientation of the molecules on the tilt cone. This results in only a modest increase in the birefringence but an anomalously large (~40º) analog rotation of the extinction direction. This unusual electro-optic response is shown to be a consequence of the molecular biaxiality.

Introduction

The fast electro-optic response of polar smectic liquid crystals has led to the exploitation of these materials in applications such as displays, optical shutters, beam steerers and phase modulators. While the response time of twisted nematic displays, where the molecules reorient in an applied field because of dielectric torques, is on the order of milliseconds [1], polar smectics, such as the chiral smectic C* phase in thin bookshelf-geometry cells, respond much more quickly, showing sub-microsecond, bistable electro-optic switching [2]. Although many studies have been carried out on the electro-optic response of such surface-stabilized ferroelectric liquid crystals (SSFLCs), several technical problems have hindered the widespread use of SSFLCs in displays, particularly, the generation of zig-zag walls in sandwich cells resulting from layer shrinkage in the smectic C* phase. Antiferroelectric liquid crystal (AFLC) phases of chiral, rod-shaped molecules [3], in which the tilt direction alternates from layer to layer, are also very promising for high-resolution displays but suffer from two intrinsic problems: (1) these materials usually have no nematic phase, typically making it difficult to align AFLCs well enough to obtain a high-quality dark state; and (2) antiferroelectric materials show a thresholdless, linear electro-optic response to small applied fields, called the pretransitional effect, which gives a dynamic contribution to light leakage under typical addressing conditions [4]. A promising SmC_A* display mode has been reported using AFLCs with a molecular tilt of θ=45°, the so-called orthoconic liquid crystal phase [5]. One of the notable features of these materials is that the ground state is optically isotropic for normally incident light. They consequently give an excellent dark state between crossed polarizer and analyzer and hence yield remarkably high contrast in test cells. The

orthoconic dark state can be electrically switched to the bright state with a speed comparable to ferroelectric liquid crystals and there are many interesting potential applications of this mode in displays and other devices requiring a fast electro-optic response [6].

The equilibrium states of the B2 phase of bent-core LC molecules are well established [7], and a variety of electro-optic behavior under application of electric field has been observed, including the electro-disclinic effect [8] and electric-field-induced chirality flipping [9]. Switching between the orthoconic ground state (optically isotropic) and field-induced birefringent states of SmC_AP_A bent-core molecules (the bilayer smectic B2 structure in which the tilted directors are anticlinic and the polarization directions are antiferroelectric in adjacent layers) has also been reported [10, 11, 12]. Here we describe the unusual electro-optic response first reported in the SmC_AP_A phase of W508, a bent-core material with a molecular tilt θ of almost 45° [13]. In the absence of applied electric field, the ground state has very low birefringence, with dark extinction brushes oriented along the crossed polarizers in focal conic domains. Upon applying a small electric field, the brushes immediately undergo a large analog rotation (~40°), accompanied by a small increase in birefringence. On further increasing the electric field, above the threshold value E_{AF-F} for the antiferroelectric to ferroelectric phase transition, the brush orientation shows little further change, gradually increasing to about 45°, while the birefringence increases steadily to its saturated value. This behavior is very different from what is typically observed in the antiferroelectric (SmC_A^*) phase of rod-like molecules, where the response below the threshold field (the pre-transitional effect) is small, and significant

brush rotation with an accompanying increase in birefringence occurs only above the transition to the ferroelectric state.

As a consequence of their molecular shape, most phases of bent-core LCs are inherently biaxial [14, 15, 16, 17]. In particular, biaxiality gives the counter-intuitive result that the apparent optical tilt angle θ_{app} (the angle between the extinction direction and the polarizers) may be different from the angle between the molecular projection and the polarizers [18]. In this paper, we develop a detailed model describing how the effective birefringence Δn and apparent tilt angle θ_{app} of a tilted biaxial smectic change in an applied electric field. Analytical solutions of the optical properties as a function of azimuthal orientation on the tilt cone confirm the key role of biaxiality in determining the electro-optic behavior of anticlinic, antiferroelectric bent-core LCs.

Results and discussion

The chemical structure and phase diagram of the bent-core mesogen W508 are shown in Figure 1a. Cells of 6 μm thick were filled with isotropic liquid crystal through capillary force and then the samples are cooled down from isotropic to the desired phase. The polarization current response to an applied triangular voltage is shown in Figure 1b. Double current peaks typical of antiferroelectric phases are observed within each half-cycle of the applied voltage, for example between A and B in Figure 1b. This indicates that the polarization is switching between tristable states, from ferroelectric to antiferroelectric and back to ferroelectric again within each half-cycle. The corresponding orientations of the molecules as a function of electric field strength are sketched in Figure 1c. A weak applied field induces a small distortion of the anticlinic structure, giving the so-called pretransitional effect [19]. In this regime, the molecules in the odd and even layers reorient on the tilt cone initially as a couple, aligning the net polarization of the distorted antiferroelectric layers along the applied field, and undergo azimuthal rotations of up to $\varphi \sim 10°$ in opposite directions that break the zero-field anticlinic symmetry. When the applied field exceeds the threshold $E_{AF\text{-}F}$, the (distorted) antiferroelectric state is unstable and the sample becomes ferroelectric (SmC_SP_F).

The electro-optic response, observed using depolarized transmission light microscopy, occurs in three main stages, illustrated in Figures 2a-f with the molecular orientation at each stage sketched in Figure 2g. When there is no applied field, the sample is antiferroelectric: the dark brushes of the focal conic domains orient parallel to the polarizers, and the overall birefringence is very low (Figure 2a). In an applied electric field below threshold, the molecules in adjacent layers undergo a small azimuthal rotation

proportional to the electric field strength. In the SmC_A* phase of rod-like molecules, this pretransitional response typically leads to a small rotation of the apparent optic axis but in W508 the extinction brushes rotate quickly through about 40° from the layer normal and then slowly approach 45°, while the birefringence increases by only a small amount (Figures 2b-e). Once the electric field strength exceeds the threshold, the sample is driven into the ferroelectric state, upon which there is a large increase of birefringence with little further change in the apparent tilt (Figure 2f). The variation of the apparent tilt and birefringence with applied voltage are plotted in Figure 3, both of which show consistent result as the observed electro-optic behavior. We will show below that this electro-optic behavior is due to the biaxiality.

The experimental geometry is illustrated in Figure 4a. The director is tilted from the smectic layer normal **z** by θ and has an azimuthal orientation φ. The cells, made of ITO glass, are viewed between a crossed polarizer and analyzer pair. The projection of the index ellipsoid onto the glass, with effective birefringence $\Delta n=n_{\parallel}-n_{\perp}$ and apparent tilt angle θ_{app}, is shown in Figure 4b. In all the switching states sketched in Figures 1c and 2g, the index ellipsoids of the odd and even layers are mirror images in the y-z plane, and have identical optical properties for light normally incident on the cell. Modeling a single layer of molecules is therefore sufficient to describe the electro-optic behavior of a SmC_A* or SmC_AP_A phase.

For the purposes of comparison, we first consider the optical properties of uniaxial molecules switching from the top to the side of the tilt cone, i.e., undergoing azimuthal rotation from φ=0° to φ=90° as sketched in Figure 4c. The dependence of Δn and θ_{app} on azimuthal angle φ in this case are derived in the Supplemental Material [20]. An example of the uniaxial response, assuming indices n_3=1.7 and n_1=n_2=1.5 typical of a uniaxial liquid crystal and a molecular tilt of θ=44°, is shown in Figure 4d. As the molecule rotates on the tilt cone, both the birefringence and the apparent tilt angle increase steadily. This behavior is typical of SmC_A* cells. For the small azimuthal rotations associated with the pretransitional effect (φ~<10°), the apparent tilt angle only reaches about 9.5°, far smaller than the saturated value eventually obtained at high fields.

If we include in the optical model the manifest biaxiality of the bent-core molecule, the electro-optic behavior is very different. The details of this derivation are also shown in the Supplemental Material [20]. The reorientation of a model bent-core molecule as a function of electric field is sketched in Figure 4e. The variation of birefringence Δn and apparent tilt angle θ_{app} with azimuthal orientation φ in this case, assuming indices n_3=1.7 along the molecular long axis **n**, n_2=1.59 along the molecular polarization **p**, and n_1=1.5 perpendicular to the tilt plane, and a tilt angle of θ=44°, are shown in Figure 4f. In the absence of applied field, where φ=0, the birefringence Δn is very low (Δn~0.004). The small azimuthal rotation (for example, φ~5°) induced by a weak applied electric field causes the birefringence to increases only slightly (from Δn~0.004 to Δn~0.018) while the apparent tilt angle increases dramatically (from θ_{app}~0° to θ_{app}~38°). Above the

ferroelectric switching threshold, the molecules reorient to φ~90°, with the birefringence Δn increasing steadily to its saturated value while the apparent tilt angle θ_{app} remains around 44°. This model is consistent with the observed electro-optic response of W508 and the analytic solution produces a result similar to that obtained in the simulation of Stern et al. [21].

To highlight the effects of the optical biaxiality, we plot the birefringence Δn as a function of apparent tilt angle θ_{app} for both uniaxial and biaxial molecules in Figure 5a. For uniaxial molecules (solid curve), the birefringence Δn increases steadily as θ_{app} increases, while for biaxial molecules (dashed curve), Δn is initially much smaller and hardly changes with increasing apparent tilt angle θ_{app} until the threshold field $E_{AF\text{-}F}$ is reached, following which the birefringence Δn increases rapidly to saturation while the apparent tilt angle θ_{app} remains around 44°. These calculations use generic values of the principal indices in order to illustrate the characteristic electro-optic behavior of biaxial molecules. The actual indices of W508, extracted by fitting the experimental Δn versus θ_{app} data shown in Figure 5b, are n_3=1.643, n_2=1.549 and n_1=1.483, with θ=44°.

In general, the nature of the electro-optic response of biaxial molecules depends critically on the magnitudes of both the molecular tilt and the refractive indices. We consider, by way of illustration, the electro-optic response of model materials with different values of these parameters. For θ=44°, n_3=1.7, n_2=1.59 and n_1=1.5, so that the biaxiality δn=0.09, the calculated response is qualitatively similar to the experimentally observed behavior. If we reduce the biaxiality, however, by lowering the intermediate index to n_2=1.55 so that

$\delta n=0.05$, the behavior of the apparent tilt angle θ_{app} and birefringence Δn resembles the uniaxial case (see Figure S.2 in the Supplemental Material [20]). On the other hand, if we increase the biaxiality, setting $n_2=1.64$ so that $\delta n=0.14$, the optical tilt approaches the saturated value 44° starting from 90° (another curious effect of the biaxiality), but the overall behavior is similar to the uniaxial result (see Figure S.3 in the Supplemental Material [20]). In other words, when $\theta=44°$, the characteristic response of W508 reported here is only reproduced by the model with $n_3=1.7$ and $n_1=1.5$, as in Figure 4f when n_2 is in a narrow range around 1.59. However, if we reduce the tilt angle to $\theta=30°$ and use these same indices, the calculated behavior resembles the uniaxial response from before, with the apparent tilt angle θ_{app} now increasing slowly to 30° (see Figure S.4 in the Supplemental Material [20]). If we increase the value of n_2, however, to $n_2=1.64$ (so that $\delta n=0.14$), this again produces the unusual electro-optic response described in this paper, where the apparent tilt angle θ_{app} increases quickly for a small azimuthal rotation while the birefringence Δn remains low (see Figure S.5 in the Supplemental Material [20]). In all cases, the model only produces this characteristic electro-optic behavior when the zero-field birefringence Δn is very small at $\varphi=0$.

Summary

Electro-optic behavior characterized in weak applied fields by a large rotation of the extinction direction accompanied by a small increase in birefringence, followed at higher field by a sharp increase of birefringence with very little further rotation of the extinction direction, has been observed in an anticlinic, antiferroelectric phase of a bent-core liquid

crystal with molecular tilt close to 45°. We have successfully modeled these observations using a biaxial description of the dielectric tensor. A prerequisite for a material to exhibit this unusual electro-optic behavior is that the projected biaxial index ellipsoid approaches a circular shape in the absence of field, i.e., that the birefringence Δn is very low when the azimuthal angle is zero.

Acknowledgement

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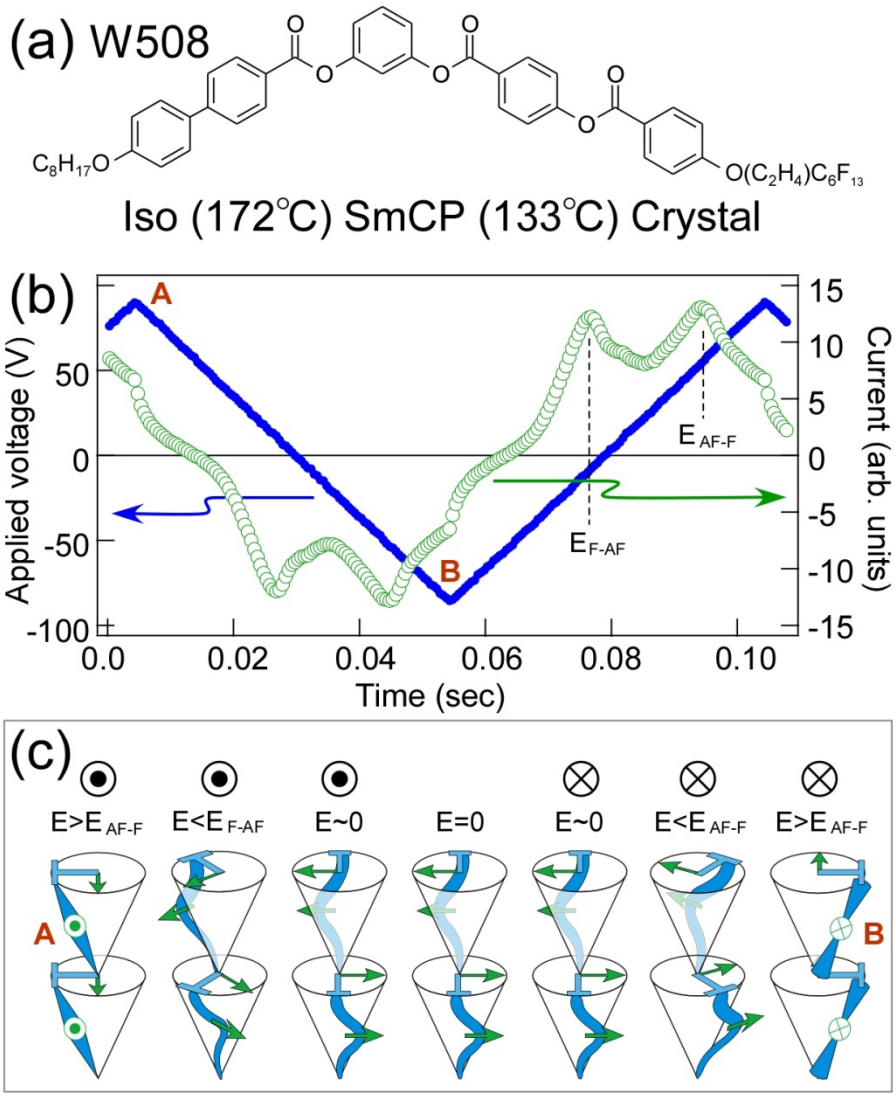

Figure 1. (Color online) Polarization current response and molecular rotation of the SmC_AP_A phase of the bent-core molecule W508 in an applied electric field. (a) Chemical structure and phase sequence of W508. (b) Polarization current response at T= 150ºC showing double peaks within each half-cycle of the applied triangular voltage (for example, from A to B). (c) Molecular reorientation over a half-cycle of the applied voltage, where the ordering evolves from ferroelectric to antiferroelectric and then back to ferroelectric. When the applied field is non-zero, the net polarization is aligned along the electric field direction. In the absence of applied field, the orientation of the tilt plane

is determined by the boundary conditions of the cell: here we show the case where the tilt plane is perpendicular to the glass substrate.

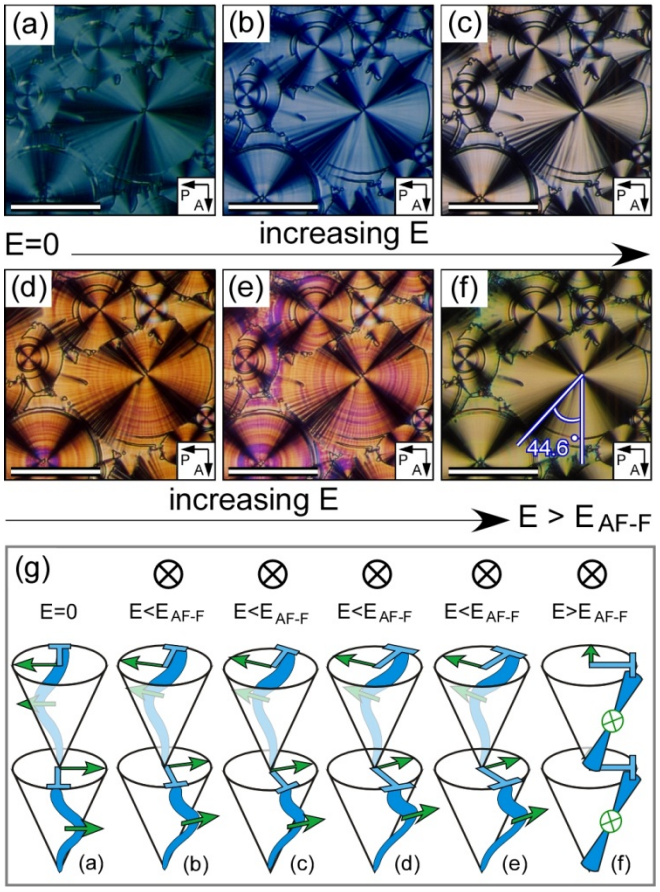

Figure 2. (Color online) Depolarized transmission light microscopy images of a 6 μm thick W508 cell at T = 150ºC. (a) The anticlinic, antiferroelectric ground state exhibits a typical focal conic texture with very low birefringence (Δn~0.017) and extinction brushes along the smectic layer normal. (b)-(e) In response to an increasing applied electric field below threshold ($E<E_{AF-F}$), the extinction direction rotates quickly by almost 40º from the layer normal and then begins to saturate. The birefringence increases slowly in this field range (from Δn~0.033 in (b) to Δn~0.066 in (d)) but is overall still very small. (f) Once the field strength exceeds the switching threshold, the birefringence increases dramatically to a saturated value (Δn~0.133). The optical tilt reaches almost 45º. The scale bars correspond to 100 μm. (g) Molecular orientations corresponding to images (a)-(f).

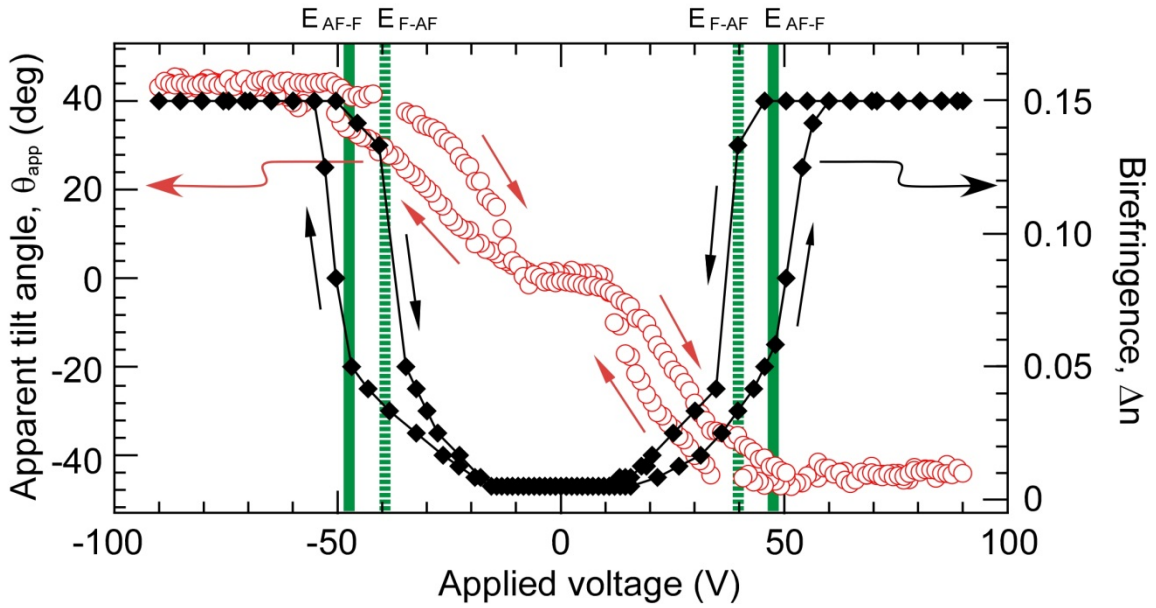

Figure 3. (Color online) Apparent tilt angle θ_{app} and birefringence Δn versus voltage applied across a 6 μm thick W508 cell at T=150ºC. Both response curves show double hysteresis over a full switching cycle. When E=0, the apparent tilt is zero and the birefringence is very low. As the electric field increases towards the switching threshold E_{AF-F}, the apparent tilt angle changes rapidly, while the birefringence increases by only a small amount. Above the threshold field, the birefringence undergoes a sharp increase while the apparent tilt shows little further change.

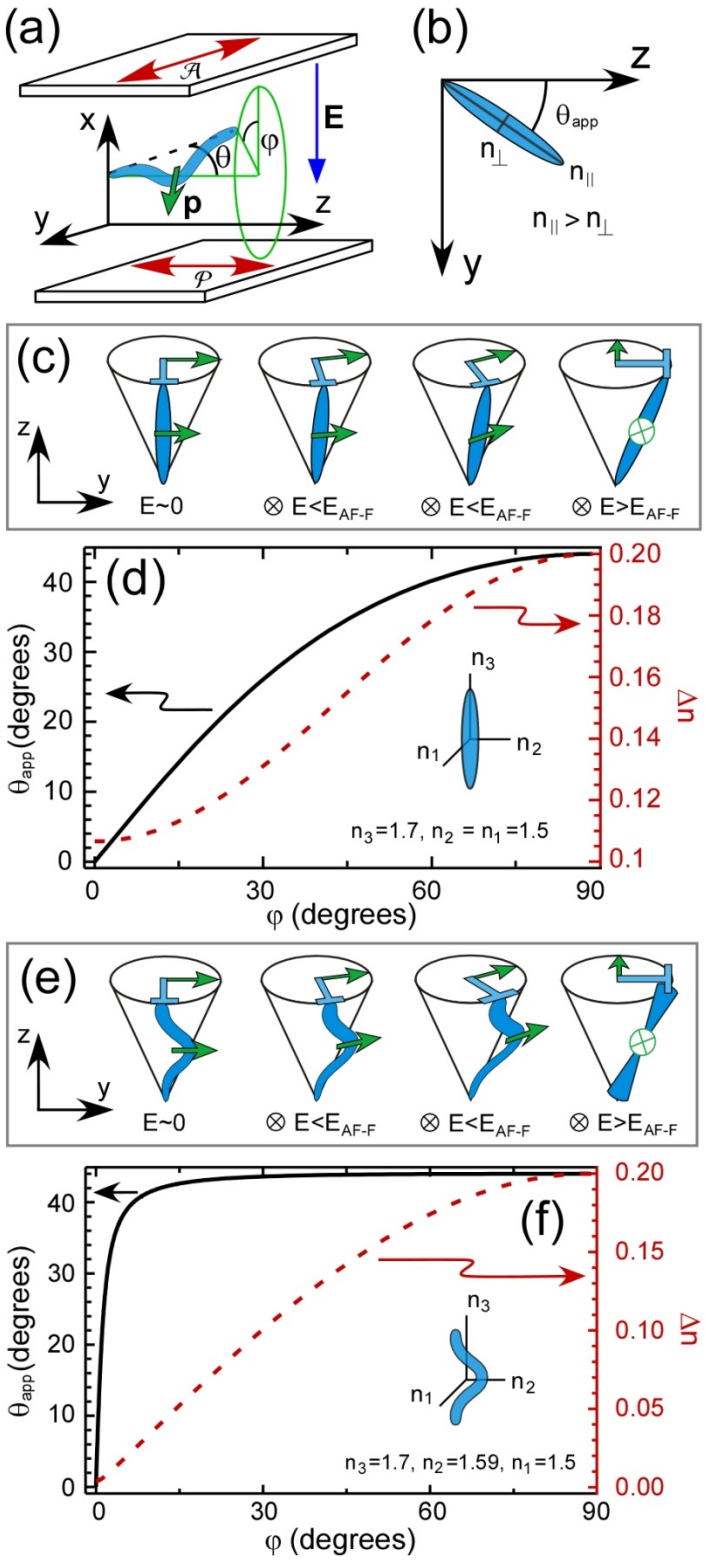

Figure 4. (Color online) Model electro-optic behavior of uniaxial and biaxial molecules. (a) Experimental cell geometry showing the azimuthal angle φ, molecular tilt angle θ and

polarization **p** of a bent-core molecule. (b) Projection of the molecular index ellipsoid in the plane of the substrate, showing the principal optical indices $n_{\parallel}$ and $n_{\perp}$ (with $n_{\parallel}>n_{\perp}$) and the apparent tilt angle θ_{app} (the angle between the z axis and $n_{\parallel}$). (c) Reorientation of a uniaxial, chiral, rod-like molecule in the SmC_A* phase in an applied electric field and (d) the corresponding calculated birefringence Δn and apparent tilt angle θ_{app} vs. azimuthal angle φ with $n_3=1.7$, $n_1=n_2=1.5$ and $\theta=44^{\circ}$. (e) Reorientation of a biaxial bent-core molecule in an applied electric field and (f) the corresponding biaxial electro-optic response with $n_3=1.7$, $n_2=1.59$, $n_1=1.5$ and $\theta=44^{\circ}$.

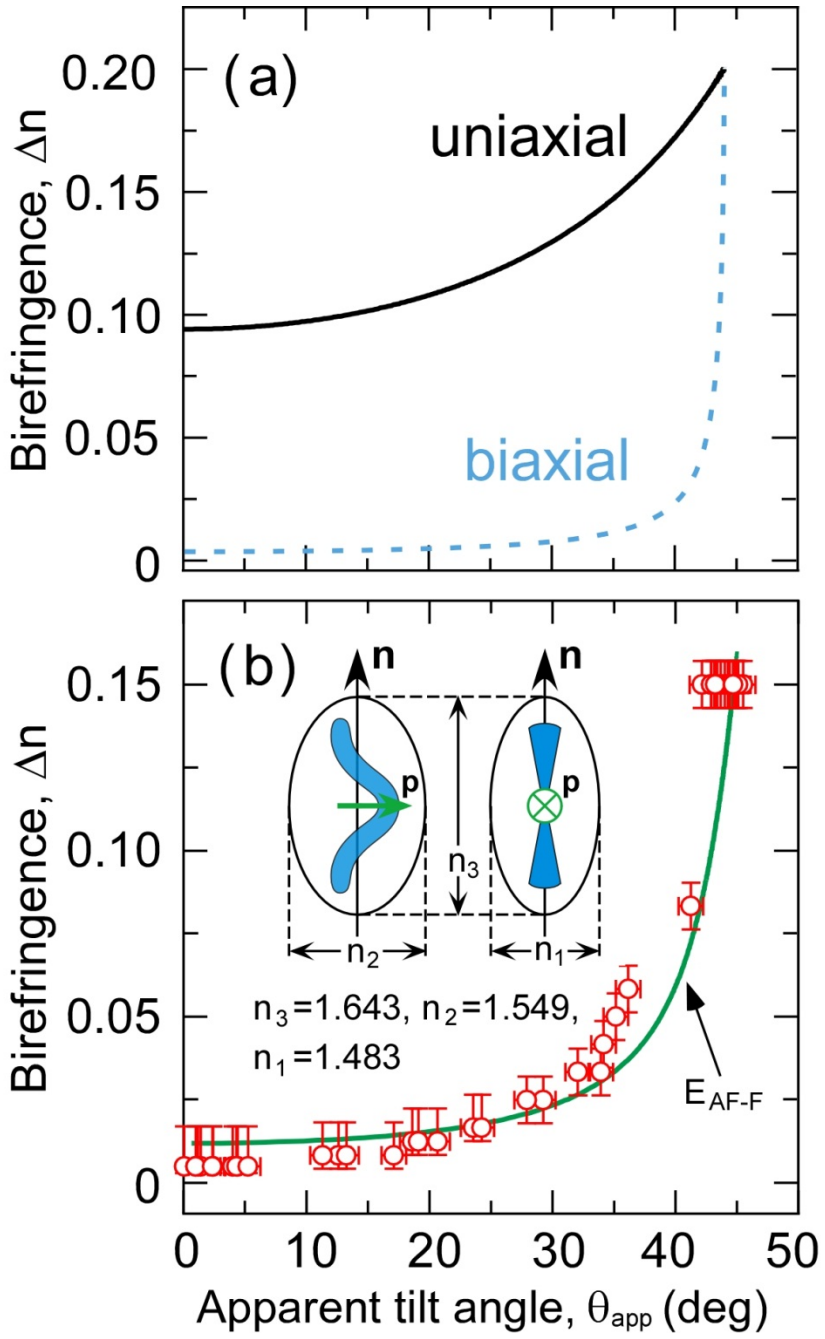

Figure 5. (Color online) Birefringence as a function of apparent tilt angle. (a) Calculated birefringence Δn versus apparent tilt angle θ_{app} for smectic phases of uniaxial, rod-like (n_3=1.7, n_1=n_2=1.5) and biaxial, bent-core (n_3=1.7, n_2=1.59, n_1=1.5) liquid crystals with molecular tilt θ=44º. (b) Electro-optic response of W508 measured in an increasing field and fit using a biaxial model. The principal indices extracted from the fit are shown in the figure.

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[20] See Supplemental Material at [URL will be inserted by publisher] for the detailed derivation of the effective birefringence Δn and apparent tilt angle θ_{app} dependence on azimuthal angle φ in tilted uniaxial and biaxial phases and the change of the effective birefringence Δn and apparent tilt angle θ_{app} corresponding to different tilt angle θ and refractive indices n_3, n_2 and n_1.

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