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SWITCHING BEHAVIOUR OF ANTIFERROELECTRIC LIQUID CRYSTALS

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We present a model of antiferroelectric liquid crystals that explains a number of phenomena observed in their switching properties. These include the pretransitional effect, the thresholded transitions between the antiferroelectric and ferroelectric states, the frequency dependence of the hysteresis loop and the origin of the v-shaped switching observed in some antiferroelectric materials.

Keywords: antiferroelectric; domains; helix; pretransitional; quadrupolar; switching; threshold; thresholdless; unwinding; v-shaped

INTRODUCTION

Antiferroelectric liquid crystals (AFLCs) [1–5] are smectic liquid crystals in which the director is at a fixed angle, θ to the layer normal. The projection of the director onto the smectic layers is known as the c-director, and is defined by an azimuthal angle, ϕ. The interlayer interaction causes the c-directors of adjacent layers to be almost anti-parallel, the discrepancy being caused by the chirality of the molecules, and giving rise to a macroscopic helical structure. Each layer has C_2 symmetry, and hence a spontaneous polarisation along the C_2 axis (perpendicular to the layer normal and c-director). In the ground state there is no net polarisation due to the anticlinic ordering between adjacent layers. For sufficiently high electric field applied along the smectic layers, all the individual layer polarisations align with each other and the field, forming the ferroelectric

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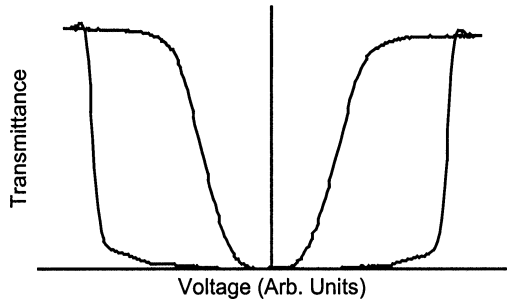

FIGURE 1 Typical quasistatic hysteresis loop of an AFLC at room temperature.

state. This field induced phase transition from the antiferroelectric (AF) state to the ferroelectric state (F) is thresholded, indicating a first order phase transition. The range of fields below the threshold is known as the 'pretransitional regime'.

Figure 1 shows the transmittance of a planar aligned antiferroelectric liquid crystal device between crossed polarisers (with one polariser along the smectic layers) as a function of applied voltage. It is clear that there is a small amount of light leakage of the antiferroelectric state in the pretransitional regime. The origin of the pretransitional effect, and of the thresholded nature of the subsequent AF to F transition is discussed in this paper. A model of the influence of defect seeded domain switching on the shape of the hysteresis loop and its frequency dependence is also presented. Finally an explanation for the formation of the twisted ferroelectric state in so-called thresholdless antiferroelectric devices is hypothesised.

Theoretical Model

Throughout this work, a one-dimensional theoretical model is used, the geometry of which is illustrated in Figure 2. ϕ_{e} and ϕ_{o} are the azimuthal angles of the c-directors in adjacent layers. However, it is more convenient to use instead the angles ϕ_{a} and ϕ_{b}, where:

$$\phi_a = \frac{\phi_e + \phi_o}{2} \qquad \text{and} \qquad \phi_b = \frac{\phi_e - \phi_o}{2}. \tag{1}$$

so that ϕ_{a} represents the local average azimuthal angle, and ϕ_{b} the type of ordering present ($\phi_{\mathrm{b}} = 0$ for the F state, $\phi_{\mathrm{b}} = \pi/2$ for AF state). A generalised expression for the free energy (of a pair of smectic layers) that has

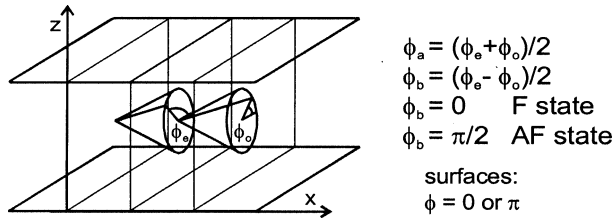

FIGURE 2 Geometry of the AFLC theoretical model.

been used for the modelling is as follows:

$$F = -EP_s \cos\phi_a \cos\phi_b + \frac{K_x}{2}\left(\frac{\partial\phi_a}{\partial x} - \frac{2\pi}{p}\right)^2 + \frac{K_z}{2}\left(\frac{\partial\phi_a}{\partial z}\right)^2 + \frac{K_z}{2}\left(\frac{\partial\phi_b}{\partial z}\right)^2 + \Gamma\cos^2\phi_b - \Delta\cos^2 2\phi_b. \quad (2)$$

E is the electric field applied across the smectic layers, P_s is the spontaneous polarisation of each layer, K_x and K_z are the interlayer and intralayer elastic constants, and Γ and Δ are the coefficients of the dipolar and quadrupolar components of the interlayer interaction energy, respectively. The first term of the expression represents the interaction of the electric field with the spontaneous polarisations in the two layers, and the final term is the interlayer interaction between the directors in adjacent layers. In order for anticlinic ordering to be preferred over synclinic ordering, Γ must be positive. The other terms represent the elastic energy stored in distortions along the helical axis and across the device thickness. In order to reduce the problem from two dimensions to one, the limiting cases of very thin and very thick devices are considered. This means that elastic terms acting in one direction only need be considered at any one time. For very thick devices, where the helical structure is present and the influence of the surfaces is very weak, the third and fourth terms are ignored, and only variations along the helical axis, x, are considered. Alternatively, for very thin devices where the helical structure is suppressed and the influence of the surface boundary conditions is very important, the second term is ignored, and only variations in ϕ_a and ϕ_b along the z axis are considered.

Supporting Experiments

The results of the theoretical modelling are supported by experimental results on planar aligned devices filled with the commercial AFLC mixture CS4001. The mixture has a pitch of 2.8 microns and forms surface stabilised and helical structures in the 1 μm and 10 μm devices used, respectively.

PRETRANSITIONAL EFFECT IN HELICAL DEVICES

The pretransitional regime in 10 μm (helical) CS4001 devices has been investigated and the details are reported elsewhere [6]. The helical structure was observed to switch by finger-like domain growth along the smectic layers to a non-helical state of greater birefringence and dielectric permittivity within the pretransitional regime, before undergoing switching to the ferroelectric state. The unwound state is deduced to be an antiferroelectric state in which the directors are approximately in the plane of the applied field [7]. By using the theoretical model, the reason for the destruction of the helix is revealed. The applied field causes a small change in the local antiferroelectric ordering (i.e. ϕ_b) within the helical structure, which results in a net polarisation along the local c-directors. This polarisation then interacts with the applied field, the torque rotating the directors towards lying in the plane of the applied field, thus distorting the helix. Above a critical field:

$$E_{critical} = \frac{\sqrt{182.4K_x(\Gamma + 4\Delta)}}{P_s p}, \tag{3}$$

the energy of the completely unwound AF state (the vertical AF or VAF state) is lower than that of the distorted helical structure, and switching from one to the other occurs via defect seeded domain growth, as observed experimentally.

AF TO F TRANSITION

If the theoretical model outlined above is applied at higher electric fields beyond the pretransitional regime, the VAF state undergoes switching to the ferroelectric state. The nature of the transition (that is, whether it is thresholdless or hysteretic) is found, by using the model, to depend on the ratio of the quadrupolar to dipolar ordering coefficients, Δ/Γ, as illustrated by Figure 3.

When the ratio of the quadrupolar and dipolar coefficients is very low, ($\Delta/\Gamma < 1/20$), the system is monostable for all applied fields (Figure 3(a)), and therefore the switching from the AF to the F state occurs continuously and thresholdlessly (Figure 3(b)). However, when $\Delta/\Gamma > 1/20$, there is a region of bistability (Figure 3(c)), and therefore the system exhibits thresholded hysteresis (Figure 3(d)). The parameters Δ and Γ have been measured in the AFLC mixture CS4001 [8], and the ratio determined to be 0.67, i.e. in the regime of bistability. In fact, the theory predicts that for values of $\Delta/\Gamma > 0.5$, the ferroelectric state is a local energy minimum state for all applied fields, although it is not the global energy minimum

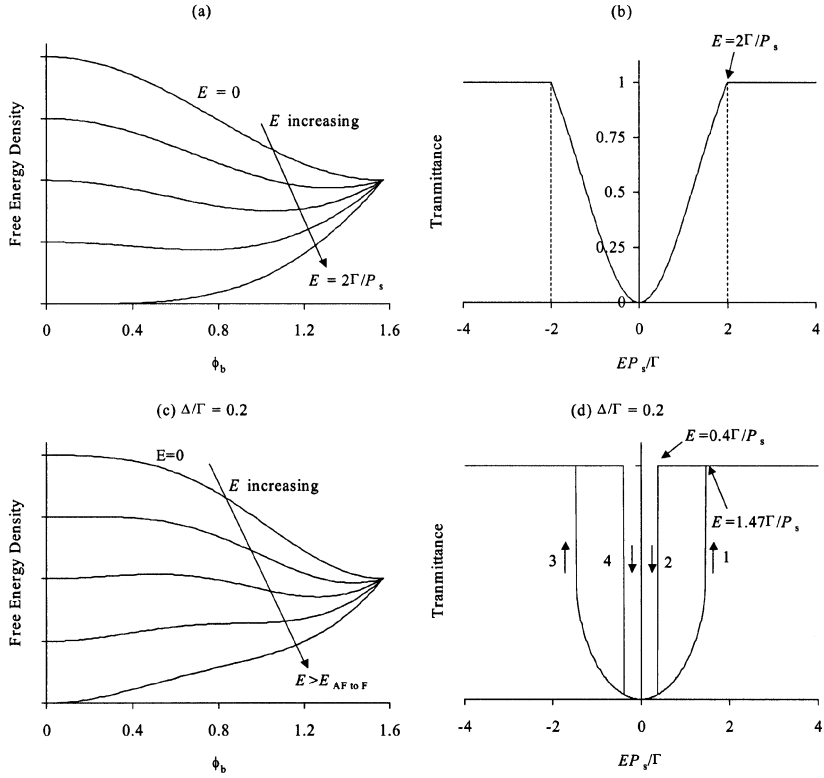

FIGURE 3 A theory that includes both dipolar and quadrupolar coupling terms can produce both thresholdless and hysteretic switching. (a) When $\Delta/\Gamma < 1/20$, the system is monostable for all applied fields, and therefore (b) the transition from AF to F is continuous and thresholdless. (c) However, when $\Delta/\Gamma > 1/20$, the system is bistable for a range of applied fields, therefore (b) the transition from the AF to the F state is thresholded and hysteretic.

below the holding voltage. This would mean that in an ideal system, once primed into the ferroelectric state, the device should in theory remain ferroelectric, and simply undergo direct F^+ to F^- switching around the smectic cone as the electric field changes sign. This is inconsistent with experimental observations of the switching behaviour of antiferroelectric liquid crystals, which exhibit thresholded hysteresis, as in Figure 1. This is due to the presence of defects and thermal fluctuations in the cell, which can seed domain switching to the lowest energy state. Therefore, in order to have a complete description of switching in antiferroelectric liquid

crystals, it is necessary to incorporate the possibility of defect seeded domain switching into the theoretical model.

DOMAIN SWITCHING

In order to model the domain switching between the antiferroelectric and ferroelectric states, some very simple assumptions about the nucleation and growth of domains are made. A triangular waveform is considered, so that the slew rate of the electric field is always of the same magnitude. As the field increases above zero, the cell remains in the antiferroelectric state until the holding field, $E_{holding}$, at which the AF and F states are equal in energy, is reached. Beyond that, defect seeded domain switching to the lower energy ferroelectric state begins. The number of domains nucleated from defects is assumed to be proportional to the difference in the electric field from $E_{holding}$, as is the speed of movement of the domain walls along the smectic layers [9]:

$$\begin{aligned} &\text{number of domains of F state per unit area} = \alpha(E - E_{holding}),\\ &\text{speed of domain growth along smectic layers} = v(E - E_{holding}). \end{aligned} \tag{4}$$

With similar assumptions for F to AF switching, and for low slew rates, the hysteresis loop predicted is shown in Figure 4(a). The results are clearly very similar to the experimental ones shown in Figure 4(d) for a frequency of 1 Hz. As the slew rate of the electric field in the theoretical model is increased, some interesting features arise in the hysteresis loop, as shown in Figure 4(b) and (c). It is clear that, again, these are qualitatively similar to the experimental results for frequencies of 10 and 25 Hz, as shown in Figure 4(e) and (f).

The changes in the hysteresis loop with frequency can be understood as follows. At higher slew rates, the domain switching from F^+ to AF (as the electric field decreases) is incomplete by the time that the field changes sign, so that a fraction of the cell is left in the F^+ state. As the domain switching continues, these parts undergo direct F^+ to F^- switching, that is, they switch around the smectic cone, without going via the AF state. In so doing, the transmittance of that part of the cell goes through a minimum and back up to its original value. The overall effect is a combination of a slow process in which the transmittance decreases slowly, and a faster process where the transmittance rapidly decreases and then increases again. This is clearly the case in Figure 4(b) and (e). At higher slew rates still, the switching is dominated by the F^+ to F^- switching and there is very little switching to the AF state, see for example Figure. 4(c) and 4(f). This provides confirmation of the assertion above that the material CS4001 is fundamentally ferroelectric. The presence of defects and thermal

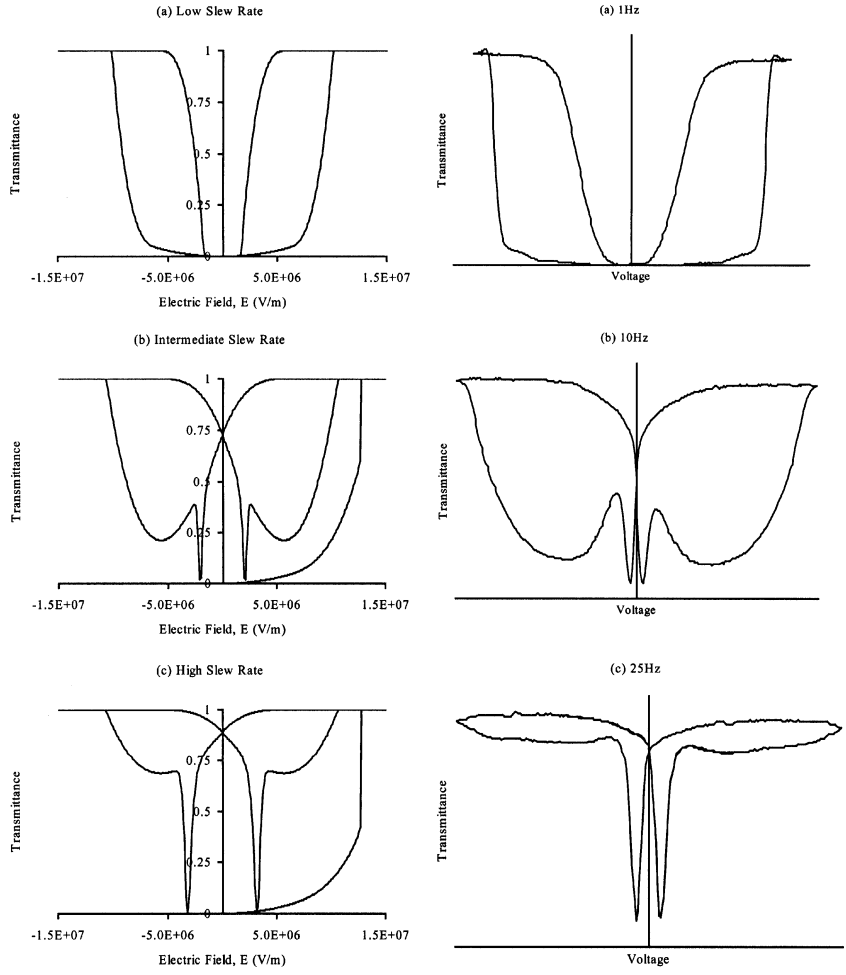

FIGURE 4 Comparison of the predicted (a)–(c) and measured (d)–(f) hysteresis loops for a range of frequencies of the applied electric field. As the frequency of the applied field increases, the shape of the hysteresis curves change so that the switching becomes more dominated by direct F^+ to F^- switching.

fluctuations in the cell change the shape of the hysteresis curves observed, in particular dominating at low frequencies.

THRESHOLDLESS SWITCHING

So far, only the switching properties of hysteretic AFLCs have been considered in this paper. In 1995, it was discovered that some AFLC

materials instead exhibit thresholdless analogue switching [10]. It may seem from the discussion above that this could be explained if the material had a very low quadrupolar to dipolar coefficient ratio. However, the 'thresholdless AFLC' mode is now widely accepted to be simply that of a twisted ferroelectric state [11], i.e. the bulk AFLC material when confined to a cell geometry forms a twisted ferroelectric structure with v-shaped switching properties. However, although the formation of the twisted ferroelectric structure has in the past been attributed to the polar influence of the cell surfaces, we have found that this is a necessary but not sufficient condition. Figure 5 shows the possible ground states that can be formed in a cell with infinite polar anchoring conditions, that is, either a twisted ferroelectric or a twisted antiferroelectric structure or both (bistability). The results are generated using the theoretical model in zero field in the thin cell limit (no helix). The phase diagram shows that in order for the twisted ferroelectric state to be formed in preference to the twisted

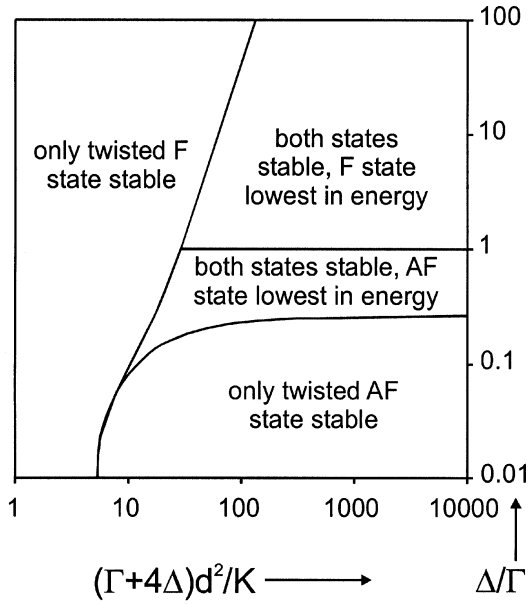

FIGURE 5 Phase diagram showing the stability of the twisted ferroelectric and twisted antiferroelectric states as a function of the cell thickness and of the ratio of the quadrupolar to dipolar ordering coefficients. The results show that in order for the twisted ferroelectric state to be energetically preferred over the twisted antiferroelectric state, either the device must be very thin, or there must be a very high quadrupolar to dipolar ordering ratio. The results also show regions of bistability, in which both twisted AF and F states are stable.

antiferroelectric state, either the cell must be very thin, or there must be a very high ratio of the quadrupolar to dipolar coefficients. Since the thresholdless mode has been reported in standard thickness cells, we conclude that the latter is the case in Refs. 10 and 11.

Frequency Effects and Priming

It is also interesting to note that for standard cell thicknesses ($\sim 3\,\mu m$), the twisted ferroelectric state will never be the only stable state: the twisted antiferroelectric state will also be a local energy minimum, although either state can be the lowest in energy overall. In these cases, either state could be lower in energy. If the F state is lowest energy, then the cell will remain ferroelectric and undergo analogue switching. If, however, the AF state is lowest in energy, then some interesting effects can occur. When a field is applied to the twisted AF state, thresholded switching to the F state will occur. When the field is removed, the device will return to the AF state, just as in a non twisted device. The switching will be hysteretic, unless the frequency of the applied field is so high that there is insufficient time for the material to return to the AF state, in which case the material will remain in the twisted F state. This is in complete analogy to the frequency dependent behaviour observed in non-twisted devices, as discussed above. It also agrees with some of the experimental observations of thresholdless AFLC behaviour. For example, it has been reported that in some materials thresholdless behaviour occurs only at high frequencies [12]. Also, a priming effect has been observed [11], in which the device switches hysteretically the first time, and from then on thresholdlessly, unless the device is left unswitched for a period of the order of minutes. In this latter case, the energies of the twisted F and AF states must be very similar, so that the return from the F to the slightly lower energy AF state is very slow.

Temperature Effects

It has also been observed that the thresholdless effect can sometimes appear at elevated temperatures, when it is hysteretic at low temperatures [12], which can be understood as follows. As the temperature increases towards the phase transition with the SmC^* phase, the dipolar ordering coefficient Γ will decrease, since it must change sign at the phase transition. The quadrupolar coefficient Δ will not change sign, therefore the ratio Δ/Γ will increase (becoming infinite at the phase transition). Therefore, provided that there is polar anchoring at the surfaces, a device that is hysteretic at room temperature should become thresholdless close to the phase transition.

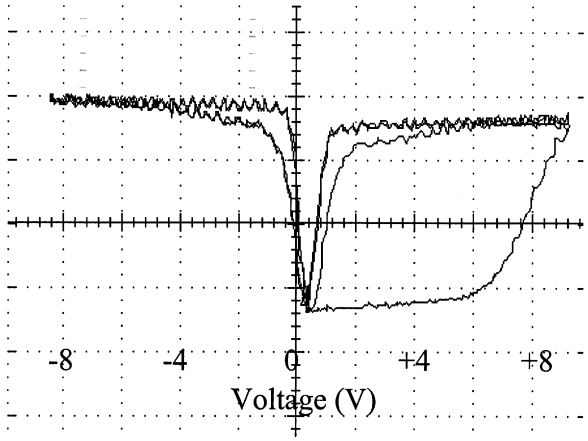

FIGURE 6 Transmittance of some parts of a 1 μm device of CS4001 between crossed polarisers in response to an applied field. The electric field primes the device from the twisted AF state to the F state, and from then on the device undergoes thresholdless switching.

Thresholdless Effects in CS4001

Our knowledge of the material parameters of CS4001, together with Figure 5, suggest that in a device with polar anchoring conditions, both twisted F and AF states should be stable, with the AF state lower in energy. In fact, we have recently observed priming and thresholdless switching in localised areas of a 1μm surface stabilised device of CS4001 at room temperature, as illustrated in Figure 6. Other areas of the device exhibit hysteretic switching of the type illustrates in Figure 1. The results suggest that isolated parts of the cell create a polar anchoring condition (whilst others don't) which has caused a twisted antiferroelectric state to form in those parts (whilst non-twisted in others). The action of the electric field is to prime the device into the ferroelectric state, from which point thresholdless switching around the smectic cone occurs.

SUMMARY AND DISCUSSION

We have presented a unified description of switching in antiferroelectric liquid crystals. The helical structure unwinds within the pretransitional regime, to form a vertical antiferroelectric state with the plane of the directors parallel to the applied field. The mechanism for the helix unwinding is the interaction of the applied field with a polarisation that is induced due to a small change in the antiferroelectric ordering. This process also causes a

small change in the optical tilt angle, therefore introducing a small amount of light leakage within the pretransitional regime.

The thresholded and hysteretic switching between the antiferroelectric and ferroelectric states can be explained in terms of a quadrupolar ordering term in the bulk free energy expression. The ratio of the dipolar and quadrupolar coefficients is such that the ferroelectric state is an energy minimum, for all applied fields. The shape of the true hysteresis curve at low frequencies, however, is dominated by the nucleation and growth of domains, which allow switching to the state of lowest energy, i.e. the antiferroelectric state below the holding voltage. At high slew rates, however, the domain growth is too slow to respond to the rapid changes in the electric field, and hence the fundamental switching behaviour is observed, i.e. the device demonstrates direct F^+ to F^- switching.

The formation of a twisted ferroelectric state in a polar anchored device (and therefore v-shaped switching behaviour) is explained in terms of a high ratio of the quadrupolar to dipolar ordering coefficients. This may be observed close to the phase transition with the SmC* phase if not at room temperature. The theory also shows regions of bistability where both twisted AF and twisted F states are stable. Where the AF state is lower in energy, frequency dependent and priming effects are predicted, in agreement with both the experimental results of others and also with our own measurements on CS4001 devices. The frequency dependence of the results is entirely analogous to that observed in non-twisted devices, i.e. the AF state (whether twisted or otherwise) is the lowest energy state below the holding voltage, therefore the material will return from the F to the AF state by domain growth when the frequency of the applied voltage wave is low enough to allow this to happen. In this case, hysteretic switching will be observed. At higher frequencies where the domain growth is too slow to respond to the changes in applied field, once primed into the ferroelectric state, the device will remain there, and undergo direct switching around the smectic cone from F^+ to F^-. The difference between the twisted and non-twisted cases lies in the resulting transmission curves. For the twisted case, the electro-optic response is v-shaped. For the non-twisted case, however, a w-shaped response is obtained (Fig. 4(c) and (f)), as the electric field must change sign before any change in the director structure occurs.

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