Unusual Electric-Field-Induced Transformations in the Dark Conglomerate Phase of a Bent-Core Liquid Crystal

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Unusual behaviour of the dark conglomerate (DC) phase seen in an oxadiazole-based achiral bent-core liquid crystal, which has not previously been reported for the DC phase of other liquid crystals, is described. Under polarizing optical microscopy, we see no domains of opposite handedness in the ground state of the DC phase. However, it shows unusual transformations when an electric field is applied to the system: On increasing the electric field, at first the domains of opposite handedness become visible and then they grow in size and slowly the sample transforms to a monochiral or single handed form which is followed by a nonchiral state at very high fields. The threshold electric fields required to achieve these changes are temperature dependent and the transformations are seen irrespective of the frequency of the applied electric field (100 Hz to 5 kHz), type of the waveform (sine, square and triangular) and the thickness (1.5 μm to 15 μm) or the geometry (planar and twisted) of the device used. Further, there is no field-induced high birefringence texture observed even though sufficiently large electric field (~22 V/μm) has been applied across the devices. The nature of the behaviour is investigated by various techniques such as optical microscopy, conoscopy, circular dichroic and Raman spectroscopies, electro-optics and dielectric spectroscopy. The possible physical phenomena behind these changes are discussed in detail.

Key words: Bent-core liquid crystal, Dark conglomerate phase, Chirality, Electro-optics,

1. Introduction

Bent-core liquid crystal research has evolved as one of the major areas of study in liquid crystal science over the last decade [1-3]. Bent-core mesogens due to their shape anisotropy exhibit a strong tendency to form lamellar phases. Usually, in such lamellar phases, in addition to the layer structure, there exists a tilt of the major molecular director with respect to the layer normal and a spontaneous polar order along the short molecular axis. These phases are normally denoted as SmCP phases (or B2 phase) and there are four distinct structures possible [4,1,2]: SmC_sP_S, SmC_sP_A, SmC_aP_S and SmC_aP_A. Here the suffixes denote the type of organization of molecules in adjacent layers (s and a refer to *synclinic* and *anticlinic* molecular tilt and S and A refer to *syn* and *anti* arrangement of the in-layer polarization direction). Sometimes the letter P in SmCP is suffixed by F/FE or A/AF; indicating the *ferroelectric* or the *antiferroelctic* order/switching observed. Recently, a SmCP phase where the molecules exhibit synclinic tilt and composed of macroscopically randomized polar domains (denoted as SmC_sP_R) has also been reported [5].

In the SmCP phases, the combination of layer structure, polar order and the molecular tilt results in intrinsic layer chirality [4,6]. Consequently, when an electric field perpendicular to the layer normal is applied to a device containing liquid crystal in $SmC_{s/a}P_A$ phases, the *anti* polar arrangement of layers switch to *syn* polar structure. During this process a simultaneous reversal in the polarization and the tilt direction takes place giving rise to a switching from SmC_sP_A to SmC_aP_S and SmC_aP_A to SmC_sP_S. Bent-core mesogens are well known for the optically isotropic phases they exhibit, which include the B4 phase [7-9], the dark conglomerate (DC) [10-19] and the dark enantiomeric (DE) phases [20]. The DC phase, which is the topic of interest of this paper, is usually found to occur below the isotropic phase. It appears completely dark or shows very low birefringence texture under crossed polarizers. On uncrossing the polarizers, it is commonly seen to exhibit chiral domains of opposite handedness in the ground state and as there is very little or no birefringence in the DC phase the chiral domains can easily be detected. There are many studies which suggest that achiral bent-core molecules may exist in chiral conformational states and under suitable conditions an enantiomeric excess (defined by $e=(n_L-n_R)/(n_L+n_R)$ where n_L and n_R are the number densities of left and right handed domains respectively) may appear spontaneously. Thus the optical activity in the DC phase of achiral bent-core mesogens is attributed to the intrinsic layer chirality or to the coupling of molecular conformational chirality to the layer chirality [21-27].

A number of studies have been carried out to understand the structure of the DC phase and it has been established that the phase consists of tilted polar smectic layers (SmCP) with relatively short interlayer correlation length and these layers curve continuously forming a saddle type structure. The spontaneous saddle-splay is associated with the saddle-splay elastic constant K_{24} being negative. Three dimensionally this looks like a structure analogous to the lyotropic-sponge and it is this spatial organization of the layers that makes the texture appear dark or optically isotropic under crossed polarizers [28,29]. The inlayer frustration caused by the orthogonal tilting of the molecular segments, which can be relieved by the saddle-splay curvature, has been suggested as

the reason for the strong tendency of some of the mesogens to form such a saddle-splay layer deformation. Under sufficiently strong electric field, the optically isotropic structure of the DC phase is usually seen to transform to synclinic and synpolar order structure (SmC_sP_S) with long range correlations and to the removal of sponge-like deformation thus giving a highly birefringent texture under crossed polarizers. Such changes give rise to a ferroelectric or antiferroelectric current response, depending on the arrangement of the layers in the ground state.

In this paper, we describe unusual electric field induced transformations observed in the DC phase of an achiral bent-core liquid crystal. Unlike that which has been typically observed for the DC phase of other bent-core mesogens, in our sample, under polarizing optical microscopy, we see no domains of opposite handedness in the ground state. However, a set of amazing transformations are observed when an electric field is applied to the device. On increasing the electric field, at first the domains of opposite handedness become visible and then they grow in size and slowly the sample transforms to a monochiral or single handed form. This state is referred as the monochiral state throughout this paper. This monochiral state, on further increase in the electric field, changes to an achiral state. No strong field induced birefringence is detected during these transformations. The circular dichroic (CD) spectroscopy gives a positive CD value for the ground state of the DC phase and shows a decrease in the chirality of the system on increasing the applied electric field. The ground state nature is further probed by dielectric spectroscopy, which indicates a $SmCP_A$ type molecular organization in the DC phase. The Raman spectroscopy, the refractive index measurement and the electro-optics confirm that there is a gross structural reorganization occurring in the DC phase when the electric field is applied across the device. We first describe the polarizing optical microscopy study of this mesophase and then provide the results obtained by optical and electrical techniques, which were carried out to understand the reason behind the observed changes. We then discuss the possible rearrangements within the structure of the mesophase which could lead to such transformations.

2. Experiment Details

The planar cells used for the experiments described below are 5-10 μm thick sandwich cells (<10 $\Omega/\square$, 30 mm^2 ITO electrode area, SE-130 high temperature polymer alignment layer) with antiparallel rubbing. The thickness of the device, averaged over a 2 mm field of view, is measured to an accuracy of ± 0.002 μm, important for the refractive index measurements which were deduced from the analysis of the reflection spectra. The temperature of the LC sample is controlled to an accuracy of ± 0.1 K using a LTS350 hot-stage connected to Linkam TMS94 temperature controller. The devices are capillary filled in the nematic phase of the material. Experiments are carried out on slow cooling (<0.5 K/min) of the sample from the isotropic phase. A Leica DM2500P polarizing light microscope is used for optical observations. An Agilent 33220A signal generator connected to home-built amplifier is used to apply an alternating electric field across the sample. Unless otherwise specified, the voltages mentioned throughout the paper are an alternating square wave of frequency 550 Hz and the magnitudes given are 0-peak values.

The circular dichroic spectroscopy was carried out in a 5 μm planar cell using Chirascan[TM] CD spectrometer. Raman spectra were collected using a Renishaw1000 Raman spectrometer which consists of a solid state laser of 515.32 nm operating at 50 mW output power, a charge coupled detector (CCD) and 50x long working distance objective. The dielectric permittivity was measured using an Agilent E4980A Precision LCR meter.

Properties of the material

The liquid crystal material under investigation is an oxadiazole based bent-core molecule, OC12-Ph-ODBP-Ph-C5. The molecular structure, phase sequence and the transition temperatures of the mesogen are given in Figure 1. The DC phase under investigation exists below a nematic phase and it occurs in both heating and cooling runs. The nematic phase of this material exhibits some unusual physical properties. Several studies indicate that there are two distinctive (possibly uniaxial and biaxial) regimes in the nematic phase [30-32]. Also, the nematic phase shows low splay (K_{11}), twist (K_{22}) and bend (K_{33}) elastic constants compared to other members in the homologues series [33,34]. It has low twist and bend elastic constants compared to calamitics [34].

The small angle X-ray diffraction study of OC12-Ph-ODBP-Ph-C5 in the DC phase was carried out by Southern *et al* [30,35]. The diffraction pattern in the DC phase shows a diffuse isotropic distribution of layers. The calculated layer spacing is ~30 Å and the calculated molecular length obtained from molecular modelling is ~34 Å. This corresponds to a molecular tilt of ~28° within a layer. Interestingly, on reducing the temperature, no change in the layer spacing was observed for up to $T_{\text{N-DC}} - T \sim 35$ K. For temperatures lower than $T_{\text{N-DC}} - T \sim 35$ K, a continuous increase in the layer spacing is measured which saturates at ~34 Å, just prior to the crystalline transition.

3. Results

Figure 1 shows the polarizing optical microscope textures seen in a planar cell in the nematic and DC phases. The DC phase exists over a wide range of temperature of ~65 K. On heating, the DC phase transforms to the nematic phase via a filament phase which exists for <0.1 K. This filament phase has been seen previously in other bent-core mesogens which possess the same aromatic core structure [30]. On cooling the sample from the nematic phase a first order transition to the DC phase is observed with a clear boundary separating the two phases (Figure 1b, 1c). In the ground state, the texture of the DC phase appears slightly birefringent and there exist small nonchiral defect regions whose size depends on the heating or cooling rate of the sample (Figure 1d). These nonchiral regions are more clearly visible in thin cells. As discussed in the introduction one of the key features of the DC phase seen in other materials is the occurrence of chiral domains. However in our sample no such spontaneous chiral domains of opposite handedness are visible at any temperature corresponding to the DC phase, on both heating and cooling regimes.

The DC phase under electric field

The behaviour of the DC phase is studied under an alternating electric field applied perpendicular to the substrates (Figure 2). Interestingly, unlike the DC phase known in the literature, no field induced birefringent state is observed even under a very high electric field (~22 V/μm). However, a constant increase in the electric field yields a new set of field induced states which have not been seen in the DC phase of other bent-core materials. These changes involve a set of threshold fields which are temperature and frequency dependent.

For a particular temperature ($T_{N-DC} - T = 3$ K) and for a particular frequency (550 Hz) of the applied waveform, on increasing the magnitude of the electric field, initially, no discernable change in the texture occurs for an electric field <8 V/μm. At $E = E_{th1} \sim 8$ V/μm, under crossed polarizers, the initial texture with low birefringence domains (Figure 2a) changes to a uniform texture which also has a very low birefringence (Figure 2b).

On further increasing the applied electric field to ~14 V/μm ($=E_{th2}$), the texture remains uniform with low birefringence, but, uncrossing the polarizers reveals domains of opposite handedness (Figs. 2c). For a fixed magnitude of the electric field, the size of these opposite handed domains depends on the frequency of the signal; the higher the frequency, the slightly bigger is the size of the domains. For example, at $E = 14$ V/μm, a change in frequency from 100 Hz to 500 Hz changes the size of the domains by ~30%. Further, an increase in the magnitude of the electric field beyond E_{th2} also assists the growth of the chiral domains (Figs. 2c-e).

On continuing to increase the applied electric field, an unexpected phenomenon occurs when E reaches ~18 V/μm; a bias towards the growth of one handed domain over the other appears (see Figs. 2f-g) and at E ~18.2 V/μm, the texture completely transforms to uniform monodomain one. That means, remarkably, that the sample attains a monochiral/enantiomeric state. The chiral nature of this enantiomeric state is confirmed by uncrossing the polarizers in opposite directions by the same angle; which shows two distinct optical states. It is interesting to note that in our experiments, irrespective of the history and geometry (planar or twisted) of the sample, the *same* handedness always takes over.

During all the above transformations that occur after the chiral domains of opposite handedness are visible, when viewed under crossed polarizers the sample still appears completely dark and rotation of the cell with respect to the crossed polarizers does not show any change in the texture.

Now, once the complete monochiral state is achieved, a further increase in the electric field results in the disappearance of the chirality in the system, leaving an achiral state. At this point uncrossing the polarizers yields the same optical state. In this achiral state, increasing the electric field further gives us a texture which exhibits low birefringence under crossed polarizers and that birefringence changes (maxima at +45º and minima at −45º from the rubbing direction) on the rotation of the device with respect to the crossed polarizers (Figure 2i-j).

The above set of transformations was furthermore examined by the conoscopy. No conoscopic pattern is observed until the sample attains the nonchiral state under electric field. After this transition, a conoscopic pattern with four dark spots parallel to the polarizers and the centre of the pattern being bright is observed (Figure 2k). This is similar to the conoscopic picture which is usually seen for orthogonal chrial smectic phases [36].

In summary, a continuous increase in the electric field applied to the DC phase of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal takes us through the following field driven states:

initial low birefringence domains $\xrightarrow{E_{th}}$ uniform, low birefringence $\xrightarrow{E_{th}}$ domains of opposite handedness $\xrightarrow{}$ chiral domains grow $\xrightarrow{}$ monochiral state $\xrightarrow{}$ nonchiral $\xrightarrow{}$ nonchiral, low birefringence.

As mentioned these field induced states occur irrespective of the type of the waveform applied (sine, square and triangular), the sample thickness (1.6 μm to 15 μm) and the geometry (planar and twisted) of the device used. However, the threshold electric fields required to achieve these field induced states are slightly higher for thinner cells (reducing the thickness of the sample by ~50% increases the threshold fields by ~20%). The POM textures of the bent-core material in a 1.6 μm planar cell are shown in Figure S1.

It is also interesting to note that, once the opposite handed domains reach the size of few micrometres, removal of the field does not take the sample back to the original texture which occurred in a fresh cell before applying the electric field. Instead, the opposite handed domains remain visible, even after keeping the cell at $E = 0$ for several hours. To remove these chiral domains, one needs to heat up the cell beyond the DC to N phase transition temperature and cool down to the DC phase, at which, the texture of the DC phase resembles that in a fresh cell. Conversely, the monochiral state achieved under electric field is stable only if the field is ON. When the sample is in the monochiral state, turning the field off brings back the opposite handed domains. Therefore, clearly the field-induced monochiral state is metastable.

Optical Experiments
In order to get a better insight into the ground state nature of the DC phase and to understand what happens to the overall chirality of the system when the electric field is applied, we carried out the circular dichroic (CD) spectroscopy of the material in the DC phase for $E = 0$ to 21 V/μm (Figure 3a). The spectra are collected from 350 nm to 550 nm. The experiment is calibrated by measuring the CD signal in the isotropic and in the nematic phase of our material. Interestingly, the CD signal in the DC phase in its whole temperature range shows positive values. (This CD spectrum does not change on reversing the direction of light propagation). These CD values are considerably lower than those usually found in the DC phase [37] and no peak is observed in the measured wavelength range. The positive CD values in the ground state of the DC phase indicate that there already exists a bias towards one handedness over the other. When an

electric field is applied across the cell in the DC phase, the intensity of the CD signal interestingly decreases. This decrease in the CD values under electric field is not continuous, rather, shows discontinuities at electric fields where the domains of opposite handedness form and transformation to the monochiral state are observed. This behaviour is depicted in Figure 3b which shows the electric field dependence of the CD signal for selected wavelengths. We simulated whether such behaviour could be due to other effects (change in the thickness of the device/alignment layer, dispersion in the refractive indices of the liquid crystal/ITO/alignment layer etc). However we find that none of those effects can produce the changes we see in the CD spectra of the DC phase under electric field. In our experiment along with measuring the CD values we also recorded absorbance spectra of the sample (in the DC phase when electric field is applied). While the CD values decrease on increasing the applied electric field no significant changes in the absorbance spectra are seen.

Also we further checked the validity of our CD results by measuring the CD spectra of a chiral mixture. The chiral mixture was prepared by doping the bent-core liquid crystal (OC12-Ph-ODBP-Ph-C5) with 2wt% of a chiral dopant (CE1, Merk Chemicals) (More detailed investigations on the chiral mixtures of this bent-core material will be published elsewhere). This chiral mixture exhibits a chiral nematic and a DC phase. As expected in the N^{*} phase of the mixture the CD values are negative (-300 mdeg in a 5 µm planar cell). The DC phase in the chiral mixture shows a uniform monochiral texture in the ground state. The CD spectrum recorded in the DC phase of the chiral mixture at $E = 0$ is given in Figure 3a-inset. Here the CD values are negative (opposite to what is obtained in our pure bent-core liquid crystal) and again take relatively low values (similar to the pure bent-core sample).

Measurement of the electric field dependence of the average refractive index, n, in the DC phase was carried out to understand the nature of the reorganization that takes place when the field is applied. The refractive index was determined from analysing the reflection spectra by the Berreman method [38]. During the experiment the rubbing direction of the cell was parallel to the plane of polarization of the incident light. The values reported are for light of wavelength 589 nm. Figure 4 shows the plot of the average refractive index versus the applied electric field. The n value measured in our experiments in the DC phase, at zero electric field, is in excellent agreement with the average refractive index deduced close to N-DC phase transition in Ref. 33.

When an electric field is applied across the device in the DC phase, the average refractive index exhibits a small increase for $E < E_{th2}$ and then starts to decrease dramatically as the electric field increases (Figure 4). This indicates that there is a gross structural reorganization occurring for $E > E_{th2}$. A considerable change in n is observed beyond $E = E_{th2} = 14$ V/µm; this is when the domains of opposite handedness become visible. For $E > E_{th2}$, n continues to decrease and surprisingly becomes ~1.61 (~n_o measured just before the N-DC phase transition in Ref. 33). A strong structural reorganization occurring in the DC phase when the field is applied is also evidenced in the Raman spectroscopy experiments.

Raman scattering spectra were recorded for the material on cooling from the nematic phase and when an electric field is applied to the DC phase. The spectra were collected from 1800 cm^{-1} to 1000 cm^{-1}. In the whole nematic and DC phase temperature range, the material showed six Raman peaks positioned at 1167 cm^{-1} (phenyl C-H in-plane deformation), 1422 cm^{-1} (C-C stretching in aromatic rings), 1496 cm^{-1} (symmetric stretching of alkyl units), 1558 cm^{-1}(C-C stretching in aromatic rings) 1608 cm^{-1} (C-C stretching in aromatic rings) and 1736 cm^{-1}(C=O stretching) (Figure S2a) (More details on the Raman spectroscopy of this material in the nematic phase are given in Ref. 34) . No shift in the peak position was observed over the entire mesophase temperature range. Tracing the intensity of the 1558 cm^{-1} and 1608 cm^{-1} peaks shows that the peak intensity increases as the temperature is lowered in the nematic phase temperature range. There is a sharp decrease in the intensity of these peaks at the N to DC phase transition (Figure S2a), consistent with the change from an anisotropic nematic to isotropic DC structure. Figure S2b shows the behaviour of the Raman peaks between 1500 cm^{-1} to 1700 cm^{-1} in the presence of electric field. On increasing the field, a new peak appears between 1558 cm^{-1} and 1608 cm^{-1}. The peaks are fitted to the Lorentz function to find the frequency of this middle peak and found that it corresponds to a wavenumber of ~1589 cm^{-1}. To assign this frequency to a molecular vibration mode the molecular structure of the material was optimized using Material Studio software and the nature of the molecular vibration responsible for a particular Raman peak was noted. The simulation is based on DMol^3 model, which is an *ab initio* method. From this work, it was determined that the Raman peak at 1589 cm^{-1} corresponds to the C-C bond stretching in the phenyl rings (adjacent to the centre oxadiazole ring) in a direction parallel to the arrow axis. The Raman spectra shown in Figure 5a and 5b for $E = 0$ and $E = 18$ V/μm respectively (= E_{th3}) clearly show an increase in the intensity of 1589 cm^{-1} peak as the field is increased. Also, the plot of the intensity of 1589 cm^{-1} versus the applied electric field shows threshold behaviour (Figure 5c). There is a strong increase in the intensity of the peak for a field up to $E \sim 9$ V/μm (~E_{th1}) and a further increase in the field does not cause significant change in the intensity of the peak.

Electrical Experiments
To explain the unusual field induced transformations of the DC phase it is important to know the in-layer molecular organization in the DC phase. Therefore, the temperature dependence of the dielectric permittivity, ε', of the material was recorded. The plot of the temperature dependence of the ε' (Figure 6), as expected, shows a clear 1st order transition between the nematic and the DC phase. It also shows that ε' is maximum at the N-DC transition and its value decreases by ~20% as we go further down in temperature in the DC phase. This indicates an antiferroelectric arrangement of the in-layer polarization direction between successive layers. There is a sharp increase in the ε' values at $T_{N\text{-}DC} - T \approx 35$ K. This corresponds to the same temperature where an increase in the layer spacing is observed by small angle X-ray diffraction. There is no DSC peak found corresponding to this temperature and no change in the texture is observed under polarizing microscope at these temperatures. The ε' was measured several times in different cells, but, the behaviour at $T_{N\text{-}DC} - T \approx 35$ K is repeatable. An electric field applied (~20 V/μm) to this lower temperature DC phase did not induce

any change in its texture, possibly because of the high viscosity of the phase at these temperatures.

To investigate the switching mechanism further a current response was measured across the cell by applying a triangular voltage of frequency 11 Hz. The experiment was carried out under the polarizing microscope to relate the current response with the textural changes. Even though there is the same set of transformations, mentioned above, occurring even under a triangular waveform, there is no significant current peak observed during these textural changes. The current response of the material when it undergoes deracemization shows two current peaks per half cycle of the applied waveform (Figure 7a). It merges into a single peak as the electric field is further increased (Figure 7b). However, the strength of these peaks is smaller than that usually reported when the DC phase transforms to lamellar phase under electric field.

4. Discussion

There are three major differences between the DC phase commonly known in the literature and that exhibited by OC12-Ph-ODBP-Ph-C5 liquid crystal. One of them is that under polarizing microscope, we see no chiral domains of opposite handedness in the ground state of the DC phase. As we discussed, the DC phase consists of SmCP structure with short range interlayer correlation length [10-19]. The absence of opposite handed domains in our sample indicates two possibilities for the ground state arrangement of the layers: The adjacent layers are either homochiral (SmC_sP_S or SmC_aP_A type), making the overall structure chiral, though the opposite handed domains are smaller than the wavelength of the visible light. Alternatively, the other possibility is that the adjacent layers are of opposite chirality (SmC_aP_S or SmC_sP_A type) building an overall racemic structure. The second difference in the DC phase of OC12-Ph-ODBP-Ph-C5 is that we see no large change in the birefringence during the various transformations that occur under an electric field. This implies that the switching in the presence of electric field happens by the molecular rotation around the director and not around the tilt cone. In other words, during switching in the presence of electric field, there is no change in the tilt sense of the layers. The third difference is that in the presence of electric field the DC phase in our sample exhibits unusual transformation states.

Altogether these results can be explained only if the ground state structure of the DC phase is SmC_aP_A. The other three possible structures in SmCP (SmC_aP_S, SmC_sP_A and SmC_sP_S) cannot explain all the states observed under electric field. Therefore, we believe that in the ground state the DC phase of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal has SmC_aP_A structure. In SmC_aP_A the layers are homochiral; therefore, any chiral domains in the ground state must be smaller than the wavelength of the visible light. The antiferroelectric nature of the layers in the DC phase is further supported by the dielectric experiments. Here the decrease in the dielectric permittivity as temperature is reduced in the DC phase can be attributed to a stronger antiferroelectric arrangement at lower temperatures. Even though a DC phase having the SmC_aP_A structure has been previously reported [14], the behaviour of our material under electric field and its properties are completely new.

When an electric field is applied to the DC phase of our sample, for fields between E_{th1} and E_{th2}, it appears that the distortion in the sponge structure is eliminated/minimized (defects texture removed) giving rise to a uniform low birefringence texture under crossed polarizers. The appearance of a C-C stretching peak at 1589 cm^{-1}, observed in the Raman scattering experiments for $E < E_{th1}$ and the existence of a threshold at $E \sim E_{th1}$ in the electric field dependence of the intensity of 1589 cm^{-1} peak (Figure 5c) corresponds to this rearrangement in the DC phase. Generally, the applied electric field assists the growth of chiral domains as the electric field reduces the free energy of the system by eliminating the distortion of the director at the boundary between the right and left handed domains. Therefore, the chiral domains which are smaller than the wavelength of visible light continuously grow on increasing the electric field and become visible for $E > E_{th2}$. Obviously, determination of these thresholds is therefore somewhat qualitative. The chiral domains continue to grow for further increase in the electric field and a monochiral state is achieved. In our experiments we always achieved the same handedness taking over irrespective of the history and geometry of the sample. This could be explained from the CD data. The CD data for the ground state of the DC phase of the bent-core liquid crystal show positive values. This implies that *in the ground state, there already exists a bias towards one handedness over the other even though the growth of one handedness over the other becomes clearly visible only under electric field*.

Once the enantiomeric state is reached, a further increase in the electric field, leads to an achiral state. This could be due to a switching from the antiferroelectric arrangement of the layers to the ferroelectric arrangement (i.e., between SmC$_a$P$_A$ to SmC$_a$P$_S$). Such a suggestion is supported because the switching between SmC$_a$P$_A$ to SmC$_a$P$_S$ occurs by the rotation of the molecules around their molecular director. This is in line with our experiments where we see no strong birefringence induced during this processes and also with the experiments of the current response, which shows double peak for $E < E_{th3}$ and for higher electric fields it changes to a single peak.

Once the SmC$_a$P$_S$ structure is reached, for a further increase in the electric field one might expect an increase the correlation length of the layers and further to the removal of the sponge deformation. However, we see no such changes even for sufficiently strong electric fields of ~22 V/μm applied across the device. It is likely that the formation of long range order and removal of the sponge-like structure in some materials and the absence of such a feature in others is related to the elastic constants of that mesogen. A study of the nature of the elastic constants in the nematic phase of our material has shown that this mesogen possesses relatively low splay, twist and bend elastic constants ($K_{11} = 8$ pN, $K_{22} = 1$ pN, $K_{33} = 3$ pN close to N-DC phase transition) [33,34]. The standard elastic approach predicts that the saddle-splay elastic constant $K_{24} \leq 2K_{11} + K_{22}$ or $K_{24} < K_{22}$ whichever is smaller [39-41]. Also, the experiments carried out on the Kerr constant, K of this material in the DC phase indicate a low value for K ($<10^{-11}$ m/V^2) [42] in the phase. Therefore, the absence of a field induced birefringence state in the DC phase of our material could be because of

the possibility of more highly negative K_{24} elastic constant and the low Kerr constant in this material.

Even though the above scenario explains much of the behaviour of the dark conglomerate phase in OC12-Ph-ODBP-Ph-C5 liquid crystal, it cannot account for the unusual decrease observed in the average refractive index, n which decreases from the average value of n to around n_o [43]. As mentioned before, this implies that the optical density of the system decreases and there is a strong structural reorganization above E_{th2}. (It is to be noted here that unlike other liquid crystal materials, this material exhibits a decrease in the optical density at the isotropic to nematic phase transition) [33]. Also, as shown in Figure 2(i-j), if a sufficiently high electric field is applied across the device in the DC phase we achieve a low birefringence texture whose birefringence changes on the rotation of the device with respect to the crossed polarizers with maxima at $+45^o$ and minima at -45° with respect to the rubbing direction. At this point, one possible description that can explain the refractive index behaviour and the one shown in Figure 2(i-j) is that the DC phase under high electric field ($E > E_{th2}$) transforms to a state where the average molecular director is perpendicular to the substrates (similar to a homeotropic state) and the low birefringence is from the secondary directors, which form a twisted structure. Such a biaxial twisted structure can explain both the decrease in the refractive index and the occurrence of a low birefringence texture which has the maxima and the minima separated by 90°. This model is supported by the conoscopic observations where we see a pattern similar to the one usually seen for the SmA* phase, only after the sample transforms to the nonchiral state under electric field.

The small angle X-ray diffraction study of the DC phase shows that at lower temperatures ($T_{N-DC} - T > 35$ K), there is an increase in the layer spacing (possibly a decrease in the molecular tilt). This supports the above idea that in the DC phase a nontilted orientation of the major molecular director is more stable and therefore application of high electric fields to the DC phase achieves such an orientation. However, as the material has negative dielectric anisotropy, the reason behind such a transformation at high electric fields is not clear and needs to be further investigated.

There is another possible way to understand the DC phase behaviour. The CD spectroscopy data of the DC phase shows that there is a decrease in the CD signal when the magnitude of the electric field applied across the device increases. This implies that there is a decrease in the chirality of the system on increasing the electric field and is analogous to the behaviour of unwinding of helix under electric field in a chiral mesophase. This is in-line with the appearance of the nonchiral state at very high electric fields. Therefore the other possible way to understand the DC phase behaviour is that it is this unwinding of some form of helical super-structure, when an electric field is applied across the cell, takes us through the intermediate states (opposite handed domains, monochiral) and finally to an achiral state. This also explains the low CD values observed in the DC phase of pure bent-core material and in the chiral mixture. However, whether the set of transformations that occur in the DC phase is purely due to the molecular reorganization within the layers or purely due to the

presence of some kind of secondary superstructure or due to a combination of these two needs further investigation. It is also interesting that the unusual electric field induced transformations described in this paper occur only in the bent-core material, which possesses the combination of alkyl and alkoxy terminal chains. Some of the homologues of this oxadiazole bent-core series, which possess alkyl terminal chains on both sides also exhibit the DC phase, however, the DC phase in those materials shows clearly visible domains of opposite handedness in the ground state. A more detailed investigation on this will be published elsewhere.

5. Summary

Unusual behaviour of the dark conglomerate phase of an achiral bent-core liquid crystal, in the presence of electric field is studied in detail. Unlike that which has been typically observed for the DC phase of other bent-core mesogens, in our sample, under polarizing optical microscopy, we see no domains of opposite handedness in the ground state. However, a set of amazing transformations are observed when an electric field is applied to the device. The nature of the DC phase was studied by various techniques and concluded that there is a gross structural reorganization occurring in the DC phase when the electric field is applied across the device leading us through amazing intermediate states. The possible explanations for the observed set of transformations that are exhibited by the material are discussed in detail.

Acknowledgements

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Figure Captions

Figure 1 Top: Molecular structure, phase sequence and phase transition temperatures of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal; Iso-isotropic, N-nematic, DC-dark conglomerate, Cr-crystalline phase. POM textures, obtained on cooling, of a 5 µm planar cell (a) at $T_{IN} - T = 60$ K, nematic phase, (b) and (c) at nematic to DC phase transition at $T_{IN} - T = 63.6$ K and (d) the DC phase texture at $T_{N-DC} - T = 3$ K. P, A and R are the Polarizer, Analyzer and the Rubbing direction.

Figure 2 POM textures of the electric field induced intermediate states seen in the DC phase for different values of the applied field of frequency 550 Hz. (a) Ground state texture of the DC phase at 0 V/µm and (b) the low birefringent uniform texture at 12 V/µm obtained under crossed polarizers. Domains of opposite handedness at (c) 14.6 V/µm and (d, e) at 18 V/µm. (f) and (g) domains of opposite handedness to the enantiomeric state transition at 18.16 V/µm. (h) Monochiral/enantiomeric state at 18.24 V/µm. Pictures (c-h) are taken under uncrossed polarizers. (i,j, (i)-inset) Achiral texture at 21 V/µm for different orientation of the rubbing direction with respect to the crossed polarizers. (k) Conoscopic pattern at 20 V/µm under crossed polarizers.

Figure 3 (a) CD spectra of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal in the DC phase at $T_{N-DC} - T = 3$ K for selected electric fields applied across the device. Inset: CD spectra of OC12-Ph-ODBP-Ph-C5+2%CE1 chiral mixture in the DC phase. (b) Electric field dependence of the CD signal of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal at different wavelengths.

Figure 4 Electric field dependence of the average refractive index, n. The vertical lines are the qualitative threshold voltages obtained from POM experiments. A strong decrease in the n values is seen above $E = E_{th2}$.

Figure 5 Raman scattering peaks 1558 cm^{-1} and 1608 cm^{-1} at (a) 0 and (b) 18 V/µm. Appearance of a new peak at 1589 cm^{-1} as the field is increased is clearly seen. (c) Electric field dependence of the intensity of 1589 cm^{-1}.

Figure 6 Temperature dependence of the the dielectric permittivity, ε' measured in a planar cell for selected frequencies. ε' decreases as the temperature is lowered in the DC phase.

Figure 7 Current response measured (a) when the sample has domains of opposite handedness and (b) in the monochiral state. $f = 11$ Hz.

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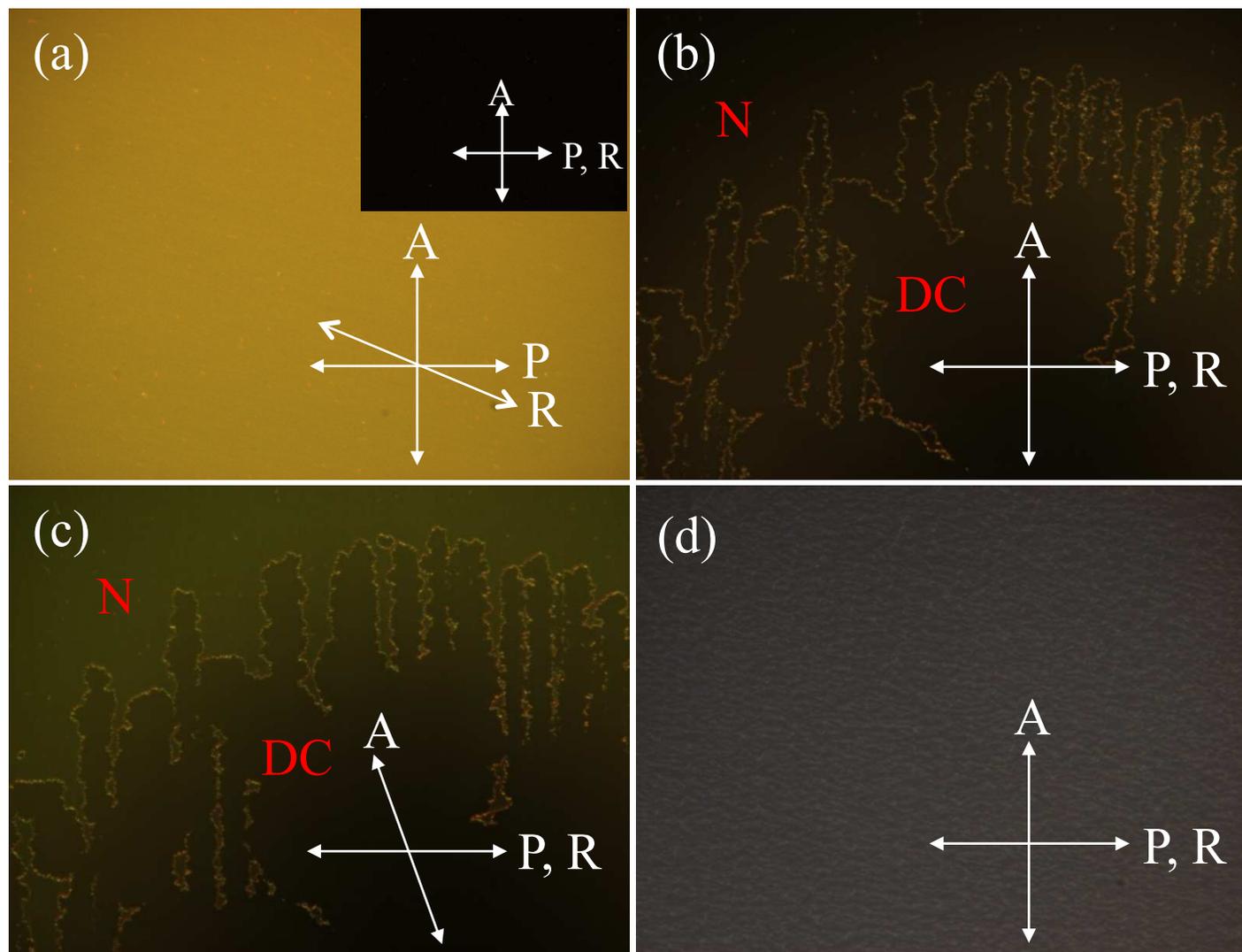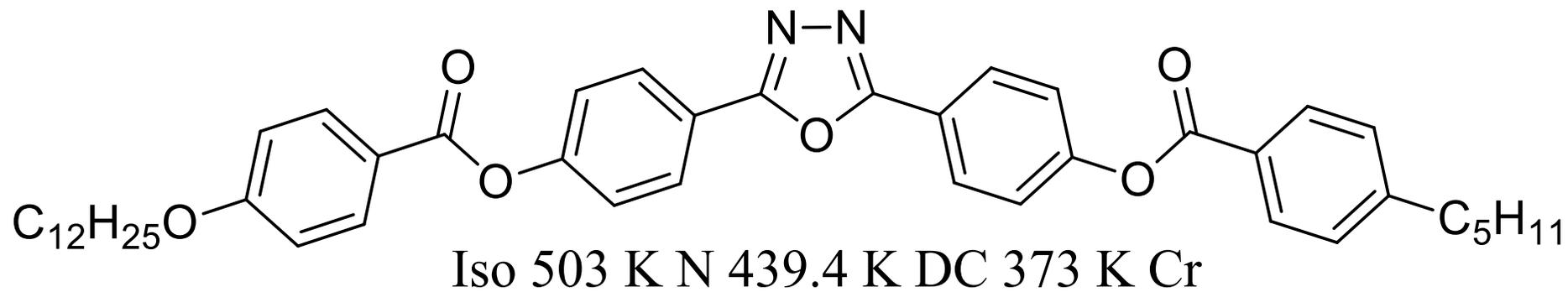
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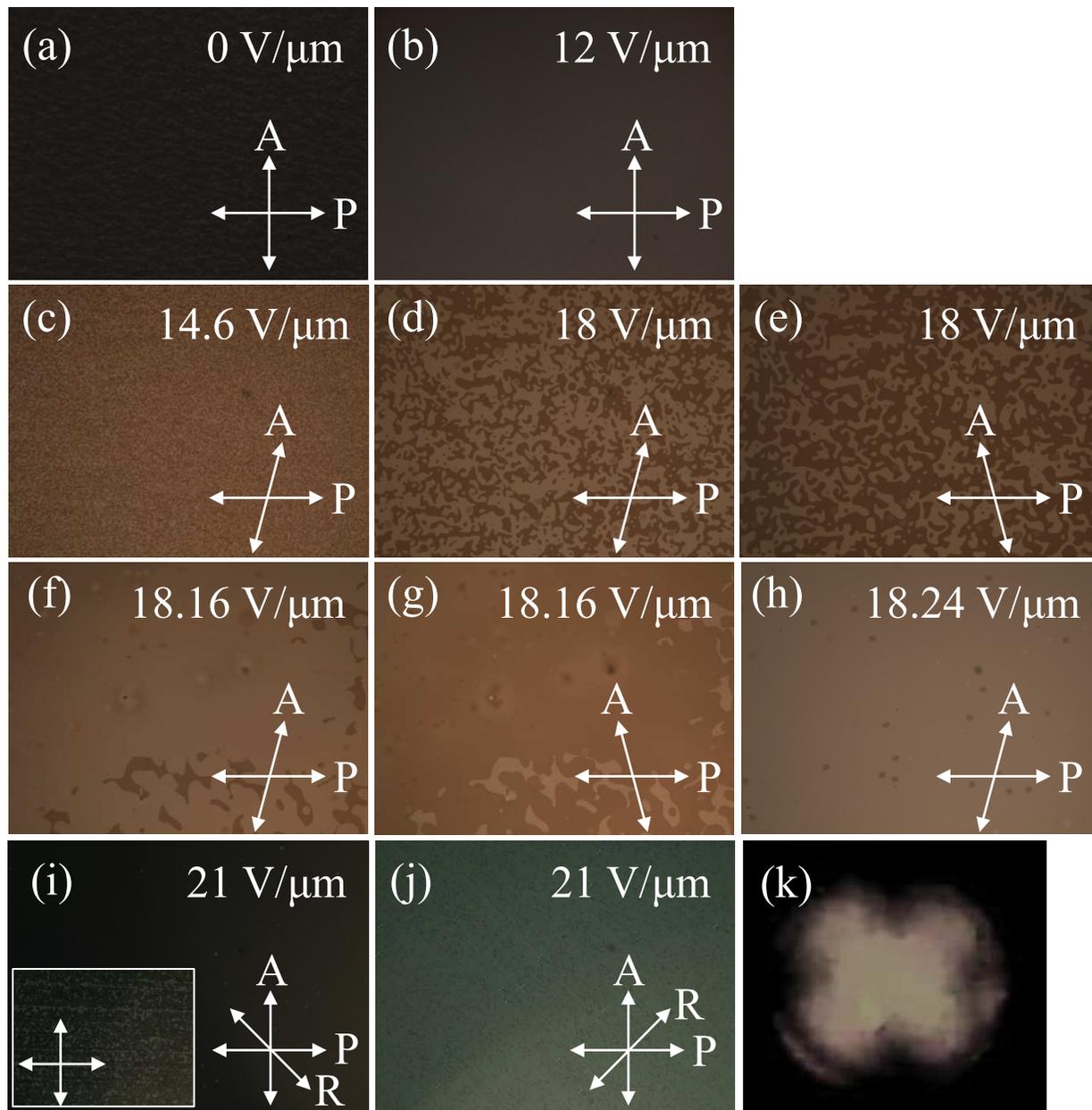
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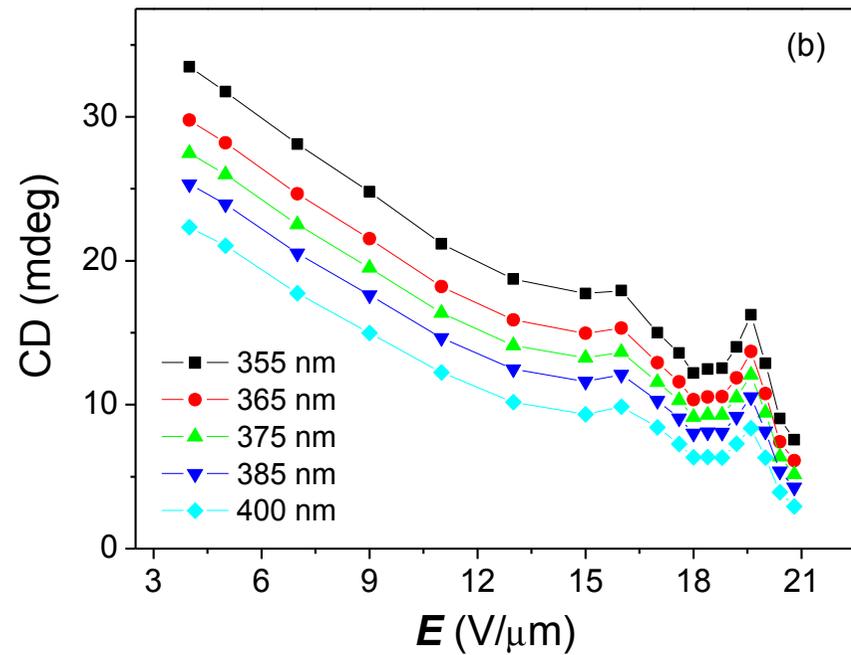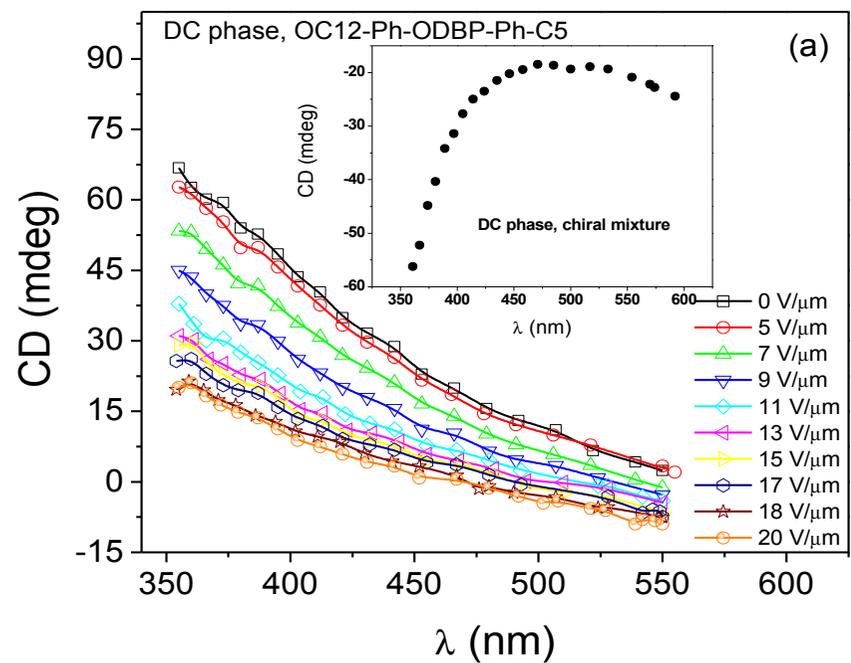
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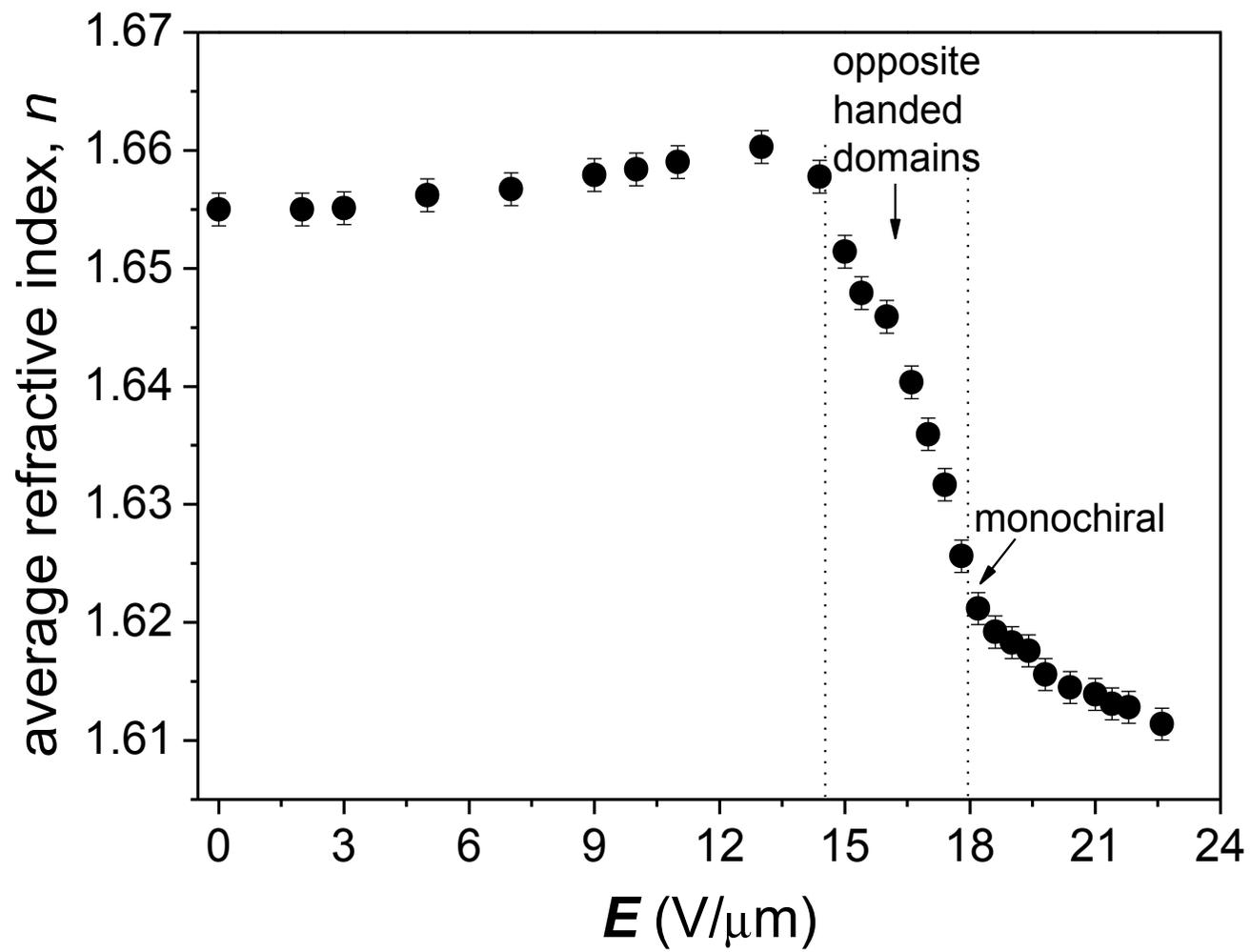
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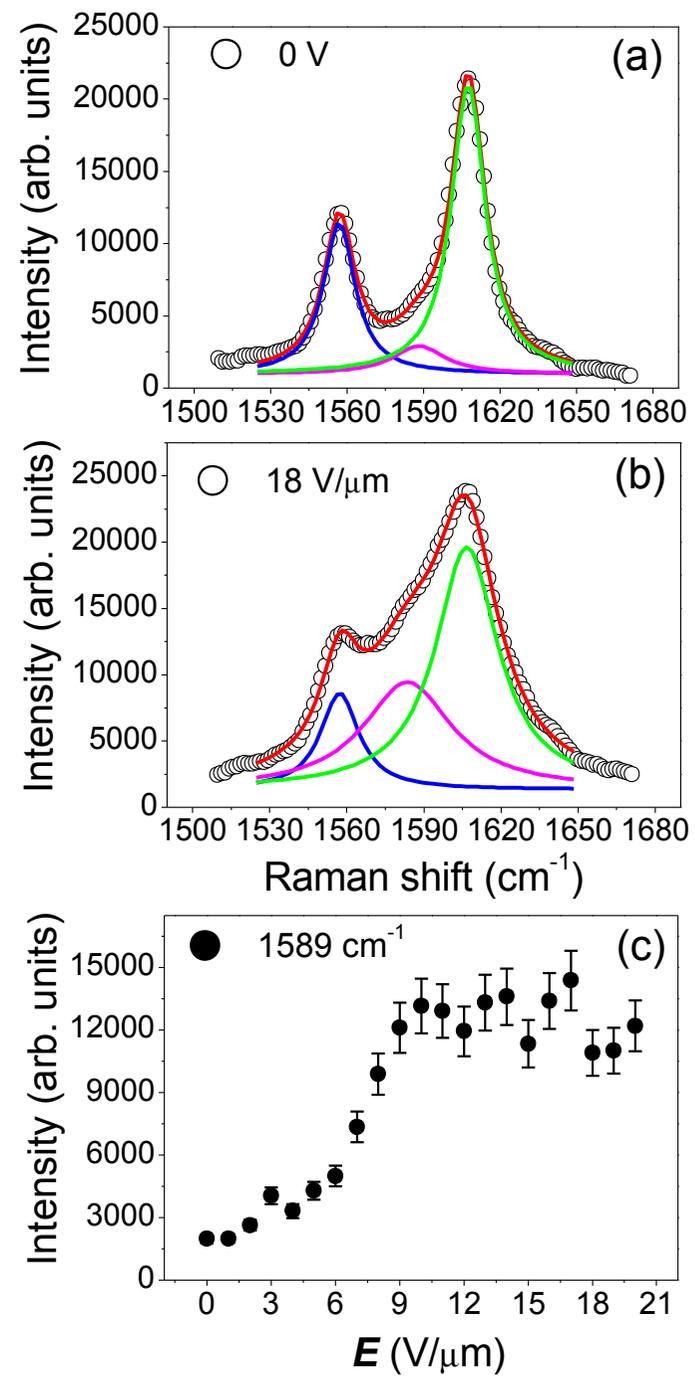
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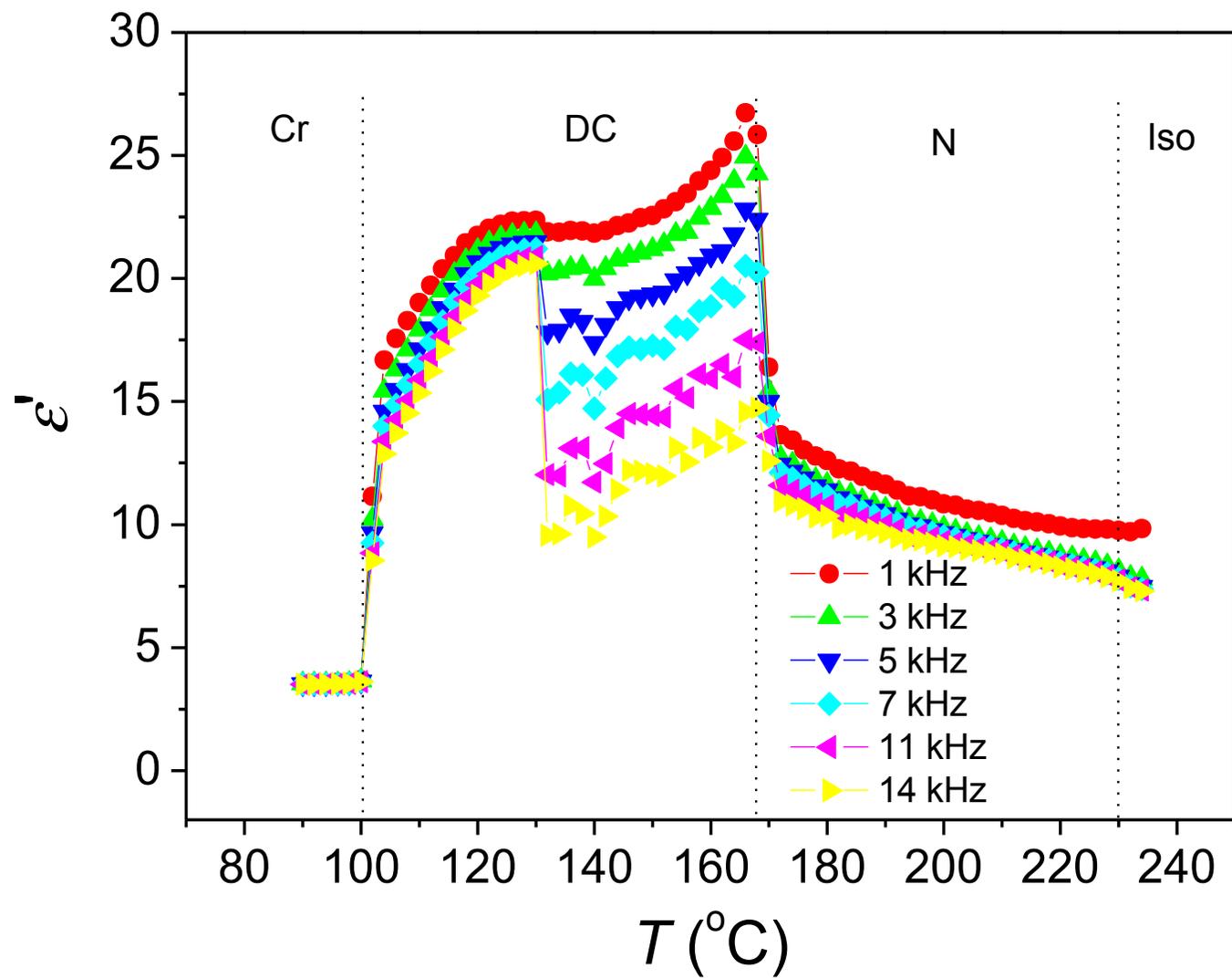
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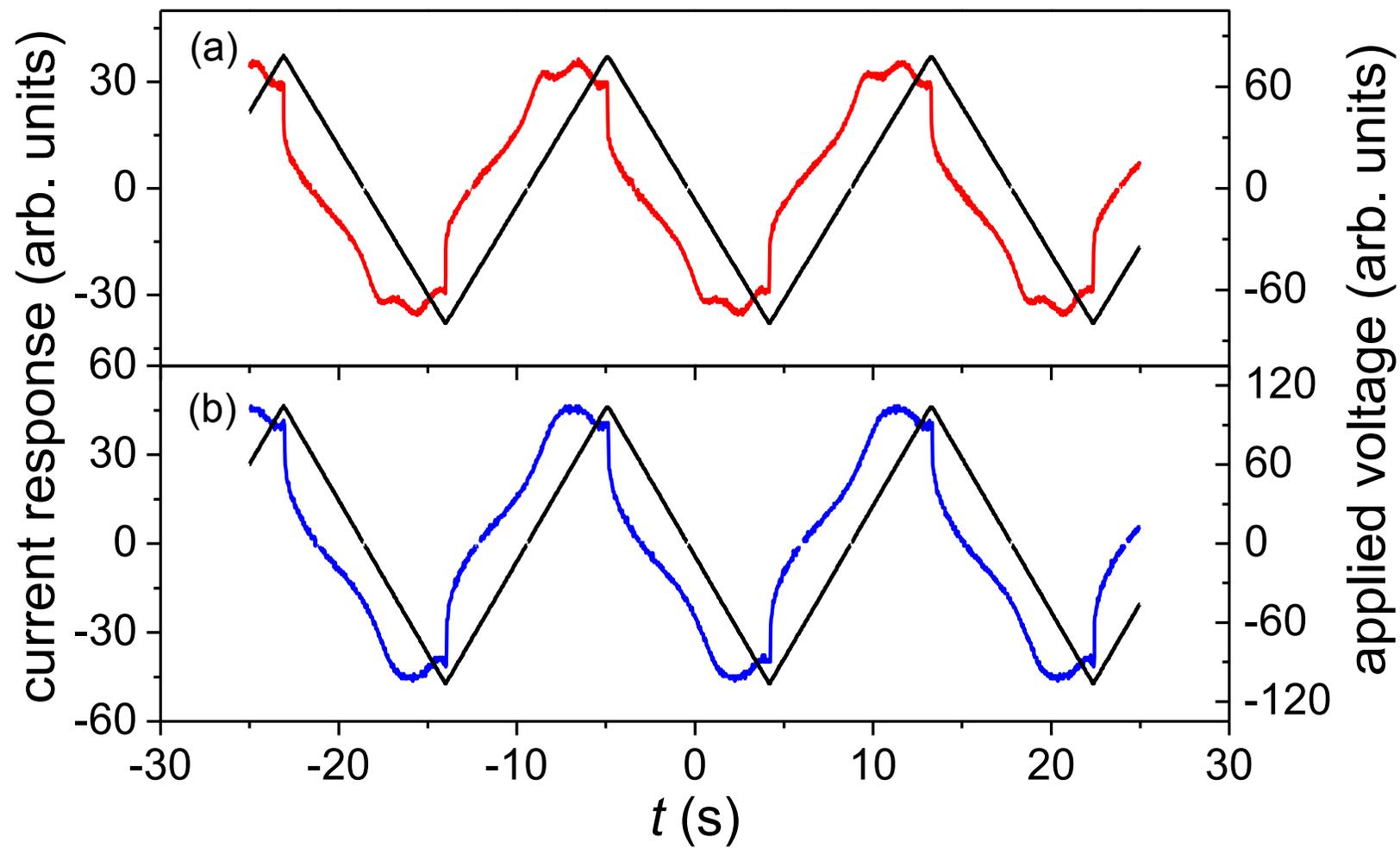
Fig. 7

Figures for SI

Fig. S1

Fig. S2