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Dark conglomerate phases of bent-core liquid crystals

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Spontaneous or induced chiral symmetry breaking in achiral systems is unusual and understanding the origin of such a phenomenon has been an important area of research for several years. The optically isotropic mesophases exhibited by unconventional liquid crystals are one of the most interesting systems to investigate spontaneous chiral symmetry breaking in liquid crystal mesophases formed by achiral moieties. The dark conglomerate (DC) phases are one such optically isotropic family of phases. In this paper, a detailed account of the tendency of bent-core mesogens to form a variety of polar smectic phases, the formation of DC phases due to layers deformations and the general optical, electrical, physical properties of the DC phases are given. An example of a dark conglomerate phase which exhibit distinct electro-optic properties is described with the nature of dynamics of the response and physical reasons responsible for such behaviour. The challenges and prospects of the dark conglomerate phases are discussed for their potential applications in novel devices.

Key words: Bent-core liquid crystals, dark conglomerate phases, chirality, polarization.

1. Introduction

An object is said to be chiral if it cannot be superimposed on to its mirror image. The origin of chiral symmetry breaking or chirality and enantioselectivity has been a research area of interest for chemists and physicists for more than a century. Understanding chirality is essential for a wide range of practical applications including drug design and organic and inorganic synthesis. In liquid crystals, the presence of chiral centre in a liquid crystal molecule can have various consequences on the properties of the mesophases it exhibits, including the formation of an intrinsic helical structure of the director field and display of spontaneous polarization [1-3].

Liquid crystallinity has been observed in mesogens with a variety of nonconventional anisotropic shapes such as X, Y, T, umbrella, hockey-stick, bowlic, etc. Amongst these, mesogens having banana shape/V-shape/bent-cores have been considered as one of the most fascinating classes due to the wide range of unique mesophases and unusual physical properties that they exhibit [4-6]. As the name suggest the bent-core liquid crystals (BCLCs) have a bent aromatic core and flexible terminal chains. Until 1996 [7], spontaneous mirror symmetry breaking was only seen in liquid crystals having optically active molecules. However, now it is well-known that bent-core liquid crystals exhibit mesophases having spontaneously chiral superstructures and polarization even though such structures are formed from achiral constituents. In the first part of this paper, a detailed account of the tendency of bent-core mesogens to form a variety of polar smectic phases is given, which then leads to the discussion on the formation of tilted polar phases and layers deformations and their general optical and electrical properties.

Orthogonal polar smectic phases

The concept of biaxiality of a SmA phase was first suggested in early 1990s. de Gennes [8]. pointed out that in a SmA phase, the properties within the layer plane will be different if one of principal axes of the magnetic susceptibility tensor $Q_{\alpha,\beta}$ is parallel to the layer normal but the transverse components of the tensor are no longer equivalent. Such a smectic phase was termed a McMillan (C_M) phase [9], in which the director is parallel to the layer normal but there is biaxial alignment of transverse dipoles in the plane of the layers. Using a mean field approximation, Brand and Pleiner [10] discussed the phase transitions involving smectic C_M and investigated the hydrodynamic and electrohydrodynamic properties of both smectic C_M and smectic C^*_M. After the first experimental observation [11] of such an orthogonal biaxial smectic phase made in a mixture of liquid crystalline side-chain polymer and a monomeric compound, for more than a decade, experimental evidence for low molar mass compounds exhibiting orthogonal biaxial smectic phases remained elusive.

The bent-core liquid crystals exhibit a strong tendency to form lamellar meophases, due to their shape anisotropy. Their kinked molecular shape creates a steric moment within smectic layers leading to polarization in the direction perpendicular to the layer normal. Depending upon the interlayer correlation of this in-layer polarization, a number of polar smectic phases could be obtained. In other words, unlike calamitics, the mesophases formed by BCLCs can exhibit ferroelectricity or antiferroelectricity even though the constituent molecules are achiral in nature.

The model of polarization in SmA phases formed by non-chiral bent-core molecules was suggested by in 1992 by Brand and Pleiner [10] and such phases are now designated as SmAP. They mainly include $SmAP_R$, $SmAP_A$, $SmAP_{AR}$, $SmAP_\alpha$ and $SmAP_F$ phases, where random, ferroelectric, antiferroelectric are represented by the subscripts R, A and F, respectively.
The first experimental evidence for the existence of a SmAP phase in bent-core liquid crystals was given by Eremin et.al [12] The compound exhibited a biaxial antiferroelectric polar smectic A ($SmAP_A$) phase with the polarization of alternating neighbouring layers being antiparallel [Fig.1]. A number of novel electro-optic effects in the $SmAP_A$ phase were reported by Nagaraj et al [13] where the reorientations in the $SmAP_A$ phase exhibit biaxial-uniaxial-biaxial transitions, with switching times of the order of ~500 µsec [13-14]. The $SmAP_R$ phase, a lamellar structure that has random arrangement of the in-layer polarization, was discovered by Pociecha et al. in 2003. [15]. Shimbo et al. [16] demonstrated that by applying an electric field perpendicular to the layer normal, biaxiality in the $SmAP_R$ phase can be induced due to a field-induced $SmAP_R$ to $SmAP_F$ transition, with a response time of the order of 100 µsec [17]. Several different versions of $SmAP_R$ phase such as the $SmAP_{AR}$ [18], which is an optically uniaxial phase but shows antiferroelectric switching, and the $SmAP_\alpha$ [19] phase, which under an in-plane electric field shows two uniaxial states separated by two biaxial states, were discovered subsequently.

The possibility of attaining a biaxial nematic phase, and then electrically switching between the minor directors, to obtain a switching time faster by a factor of at least 100 than in a uniaxial nematic phase, had been a topic of profound interest for many decades. Now, the possibility of variety of orthogonal polar smectic phases in bent-core liquid crystals, attracted a lot of attention: although the biaxial nematic phase proved elusive, the same advantage of ultra-fast electro-optic switching should be possible with in the biaxial SmA phases present in BCLCs. Also, materials in the $SmAP_R$ and $SmAP_A$ phases proved to align readily, as would be expected for the biaxial nematic. The biaxial nematic and SmA phases have orthorhombic symmetry, and hence have an **n**-director that is the statistical average of the long molecular axes, and an **m**-director parallel to one of the principal perpendicular axes [Fig. 1a]. We can define a dielectric biaxiality $\partial\varepsilon$ as the dielectric constant difference between the two perpendicular components of the dielectric tensor. Although the biaxial nematic is subject to a conventional electro-optic response of the **n** director coupling an applied electric field to the uniaxial anisotropy $\Delta\varepsilon$, the fast electro-optic switching of the biaxial nematic phase is due to reorientation about the **n**-director, through coupling between the dielectric biaxiality and $\mathbf{E}^2$. For the biaxial SmA phases, switching of the **n**-director is hindered by the layers, and only motion of the biaxial axes is found. Importantly, the ferroelectric coupling of **E** polarity of the SmAP phases is much stronger than the $\mathbf{E}^2$ coupling to the dielectric biaxiality, and the switching speed is far faster still, due to the much higher switching torque.

From an application point-of-view, a number of bent-core liquid crystals have been synthesized to exhibit the $SmAP_F$ phase: the first experimental evidence for the existence of a spontaneous ferroelectric phase with orthorhombic layers was given by Reddy et al. in 2011 [20]. Recently, an optical phase modulator based on the $SmAP_F$ phase has been demonstrated [21], where the applied electric field couples to the polarization and changes the effective birefringence without affecting the director orientation.

Tilted polar smectic phases

Bent-core liquid crystals, in addition to exhibiting a strong tendency to form lamellar mesophases, they also show an affinity to form structures, where the director tilts with respect to the smectic layers in a smectic C type fashion. Usually, the tilt plane is perpendicular to the **m**-director and average bend of the molecules. In many cases, such structures also show spontaneous polar ordering coplanar to the smectic layers in the direction perpendicular to a tilt of the major director with respect to the layer normal. The combination of layer structure, polar order, and tilt results in internal layer chirality in polar tilted smectic phases. In such a system, the polar vector (**b**), layer normal (**l**), and the tilt angle (θ_C) are related by ($\mathbf{l}\times\mathbf{n}\sin\theta_C = \pm\mathbf{b}$). The tilted polar smectic C phases are denoted as SmCP phases [Fig. 2]. There are four distinct structures possible; SmC_SP_F, SmC_SP_A, SmC_AP_F, and SmC_AP_A, where synclinicity, and anticlinicity of the tilt are represented by the subscripts S and A respectively, and ferroelectricity and antiferroelectricity of the polarisation are represented by the subscripts F and A, respectively. Chirality emerges in SmCP phases in layers as a consequence of tilt and in-layer polarization; this is known as layer chirality. The layer chirality provides a stronger coupling, therefore is more readily transferred over hundreds of micrometre distances. Both computer simulations and experimental investigations have established that BCLCs exhibit chiral conformations [22-24]. The coupling of layer chirality with the molecular conformational chirality via diastereomeric interactions leads to spontaneous chiral symmetry breaking in tilted, polar lamellar mesophases. For the SmC_SP_A and SmC_AP_F phases, the chirality in each layer is equal and opposite, and so the phase structures are inherently racemic. However, there is a net chirality for the SmC_SP_F and SmC_AP_A phases [Fig. 2]. Moreover, conglomerates of chiral domains were also found in apolar SmC phases [25-26] with only local polar domains (SmC_SP_R phases) formed by some bent-core mesogens.

When an electric field is applied to SmCP phases, two ways of reorientations are possible: rotation of molecules around the layer normal (or tilt cone) and rotation around the major director **n**. Usually, only those field-induced states that preserve the total chirality of the system are observed experimentally. In terms of applications of the SmCP phases, some of these phases show sub-millisecond electro-optic switching time due to the presence of the ferroelectric spontaneous polarization. Nevertheless systems using such phases are yet to be sold commercially due to problems associated with alignment and obtaining defect-free cells.

2. Dark conglomerate phases

The dark conglomerate (DC) phases, as the name indicates, are optically isotropic phases that exhibits conglomerates of macroscopic chiral domains. The internal structure of such phases consist of polar smectic layers with relatively short interlayer correlation length. On slightly longer length scales, the layers curve continuously forming a saddle-splay type structure [27]. The in-layer frustration caused by orthogonal tilting of the molecular segments can be relieved by the saddle-splay curvature: in three dimensions, the DC phases have significant negative Gaussian curvature. Depending on the local structure, the DC phases are classified as liquid crystalline sponge-like phases [28-37] and Helical Nano-Filament (HNF) phases or B4 phases [38-40]. In addition to these, a number of DC phases with intermediate or distinct nanostructures have been observed [41-48]. Some of them exhibit distinct electro-optic switching including switching between opposite chirality and switching between modulated smectics and DC phase structures, driven by the applied electric field. The microscopic texture of the DC phases appears completely dark under crossed polarizers. On uncrossing the polarizers, the phase usually exhibits chiral domains of opposite handedness in the ground state, which is readily observed from the circular dichroism of the DC phases as there is very little or no birefringence. It is the internal sub-wavelength structures of the director formed with the spatial arrangement of the layers that make the microscopic texture appear isotropic, and hence dark under crossed polarizers.

The sponge-like phase

The sponge-like dark conglomerate phase is formed by strongly deformed fluid smectic layers and is comprised of disordered focal conic domains. The three dimensional structure of this phase is analogous to the sponge structure [Fig. 3] common to lyotropic liquid crystals [43]. Generally, applying a sufficiently high electric field to the sponge-like phase leads to the removal of the sponge structure and produces a highly birefringent texture under crossed polarizers. This is due to the transformation of the structure to a synclinic and ferroelectric order (SmC_SP_F) that has long-range interlayer correlations [44,45].

The HNF phase

The HNF phase exhibits crystallized aromatic segments organized into helical nanoscale filaments, separated by the disordered alkyl chain segments. The phase has in-plane hexatic positional ordering of the layers, which is of a short-range. The phase reflects blue wavelengths, which has been explained as being due to the presence of a super-structural twist present in these systems [46] The HNF phase shows second harmonic generation, indicating the existence of polar order in the phase but without electro-optical switching.

3. Unusual electro-optic response of a sponge-like DC phase

Generally, applying a sufficiently high electric field to the DC phase, transforms the structure into a birefringent SmCP structure. However, below is an example of a DC phase observed in an oxadiazole based bent-core liquid crystal in which the electro-optic behaviour of the DC phase under an electric field corresponds to a number of structural changes [53]. They lead to unusual changes in physical properties and transformation where the overall sponge-like structure of the DC phase remains intact even under high electric fields approaching the dielectric breakdown limit [54].

3.1 Experimental

The samples were formed from glass etched with ITO electrodes on opposing surfaces, onto which was deposited high temperature polyimide planar alignment layers with antiparallel rubbing. A cell spacing of 5 to 10 μm was defined using plastic spheres. The temperature of the sample was controlled using a Linkam THMS600 hot stage connected to a T95 temperature controller. Slow cooling (<0.5 ^{o}C/min) was used for all experiments. An Agilent 33220A signal generator connected to a home-built amplifier was used to apply electric fields across the sample. A Leica DM2500P polarizing light microscope was used for optical observations. The small angle X-ray scattering experiments were conducted at B26B on the DUBBLE beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble France. The X-ray wavelength used was 1.03 °A and the beam diameter was 0.3 mm. Dielectric spectroscopy was carried out on devices with <15 Ω/□ ITO electrodes. Raman spectra were collected using a Renishaw 1000 Raman spectrometer (Renishaw plc, Glourcestershire, UK) which consists of a solid state laser of 515.32 nm operating at 50 mW output power, a charge coupled detector and a 50x long working distance objective.

3.2 The bent-core liquid crystal

The liquid crystal material investigated was an oxadiazole-based bent-core molecule, OC12-Ph-ODBP-Ph-C5. The molecular structure of the mesogen is given in Fig. 5(a). The DC phase under investigation exists below a nematic phase and it occurs in both heating and cooling runs. The nematic phase of the material shows low splay (K_{11}), twist (K_{22}) and bend (K_{33}) elastic constants compared to other members in the homologues series. The molecule has a ratio of polarisability anisotropy to the average as $\frac{\Delta\alpha}{\bar{\alpha}}$ ($\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}, \bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$) ~0.47 and a high biaxiality of the polarisability tensor with $\frac{\partial\alpha}{\bar{\alpha}} = +0.25$ ($\partial\alpha = \alpha_2 - \alpha_1$, α_1 being along the shortest molecular axis). Assuming that the phase biaxiality order parameter C for the SmCP phase is equivalent to that of a typical smectic C [55], the optical biaxiality is of the order of half the uniaxial nematic birefringence ($\partial\alpha \approx 0.4$).

3.3 Results and Discussion

When an electric field was applied across the sponge-like DC phase of the OC12-Ph-ODBP-Ph-C5 liquid crystal, no observable change of texture was observed for fields below 8 Vμm^{-1}. At **E** ~ 8 Vμm^{-1}, the initial texture with low birefringence defects changed to a uniformly dark texture [Fig. 5(a)] under crossed polarizers. On further increasing the field to ~12 Vμm^{-1}, the texture remains uniform and dark, but uncrossing the polarizers revealed ~5 to10 μm in size domains of opposite handedness [Figs. 5(c,d)]. Further continuous increase of the applied electric field caused these domains to coalesce and grow to form larger domains with smooth boundaries [Figs. 5(e,f)]. Further increase of the electric field, **E** to 15 Vμm^{-1}, resulted in the disappearance of the chiral domains, leaving a uniform achiral texture across the entire field of view. Uncrossing the polarizers at this point in opposite directions yielded the same optical state.

The small angle X-ray scattering corresponding to the above textural changes showed no significant changes in the d-spacing on increasing electric field [Fig. 7]. The FWHM followed the d-spacing trend, although the amplitude of the diffraction peak remains constant. The measurement of dielectric permittivity as a function of applied electric field showed a slow doubling from $\varepsilon' \sim 26$ to $\varepsilon' \sim 59$ [Fig. 8].

These results imply that, when an electric field is applied to the DC phase of OC12-Ph-ODBP-Ph-C5, the dipoles initially align parallel to the applied electric field due to strong molecular biaxiality. This causes the observed size increase of the conglomerate domains that become visible only after a threshold field is superseded. This argument is supported by a small increase in the dielectric permittivity observed during these changes [Fig. 7a] and the increase in the strength of a C-C stretching peak at 1589 cm^{-1}, observed in the Raman scattering experiments [Fig. 7b]. The chiral domains continue to grow with further field increase until an enantiomeric state is achieved. Once the enantiomeric state is reached, further increase of the electric field leads to an achiral state. This is due to a switching from the antiferroelectric arrangement of the layers to the ferroelectric arrangement (switching between SmC_AP_A to SmC_AP_F) [54]. This implies that the collective reorientation due to the polarity of the phase occurs by the rotation of the molecules around their long axes and not around the tilt cone, which is in line with the small change (1%) in periodicity observed by SAXS [Fig. 7]. Let us represent the spontaneously saddle-splayed layers of the DC phase as a sphere for the purpose of visualisation such that the layer normal is pointing outward at each point and is perpendicular to the surface of the sphere for the ground state of the DC phase. At the 'poles', the average orientation of molecules is vertical and at the 'equator' the average orientation of the molecules is horizontal [54]. For such as configuration, a low electric field is not sufficient to cause any layer reorientation, hence it remains isotopically distributed. In this situation, the molecules at the equator align along the field direction whereas those at the poles do not reorient since the field is normal to the polarization. The director at the poles is surrounded in all directions by layers curving away. Any field-induced elastic distortion is balanced at the pole on all sides, and the poles remain unchanged for even high fields. Such a reorganization induced by the applied electric-field coupling to the in-layer polarization produces an optic axis parallel to the field direction and the total refractive index will be lower than the average refractive index of the undistorted system [Fig. 7a], if the local optical biaxiality of the DC phase is positive. Such a structure can explain the unusual decrease in the average refractive index observed in the system on increasing electric field.

A study of the nature of the elastic constants in the nematic phase of the material has shown that the OC12-Ph-ODBP-Ph-C5 mesogen possesses relatively low splay, twist, and bend elastic constants (K_{11} = 8 pN, K_{22} = 1 pN, K_{33} = 3 pN close to the N–DC phase transition). The standard theoretical elastic approach predicts that the saddle-splay elastic constant $K_{24} = 2K_{11} + K_{22}$ or $K_2$4 < K_{22}, whichever is smaller. Therefore, the absence of a field-induced complete deformation of the sponge-like structure of the DC phase of certain materials could be because of the possibility of a more highly negative K_{24} elastic constant in them. Alternatively, it is also possible that the sponge-like structure must be retained because of the lack of electrical torque acting at the poles of the structure [54].

4. Prospects of the DC phases

Liquid crystals are immensely useful opto-electronic materials. Due to the very nature of the nematic phase, this liquid crystal phase is not ideal for all photonic device applications. Some of the major limitations associated with such devices include difficulty in controlling surface anchoring, strong scattering effects and polarization-related sensitivity of materials. Therefore, optically isotropic liquid crystal phases have been of major research interest for integrated optical modulators such as optical waveguides and for fibre-optic core, liquid crystal phase gratings and liquid crystal based tuneable lenses [Fig. 8]. The possibility of obtaining electric field-induced focus change via the change of the focal power of the liquid crystal layer in the DC phase is given in ref. 56. Unlike regularly used nematic liquid crystal devices, the optically isotropic nature of the DC phase means that alignment is no longer an issue. There are no contrast losses due to scattering, no requirement for alignment layers (therefore ease of fabrication) and no polarization sensitive effects.

The DC phases are model systems to understand chiral domain growth, coarsening, and scaling hypothesis and also to investigate generating and controlling chiral symmetry breaking in achiral condensed matter systems. Chirality tuning in an achiral system by applying electric field of different strengths and frequencies is important for the applications in chiro-optical and nonlinear optics devices. In addition, the DC phases having the helical nanofilament structures represents interesting materials for a variety of other optoelectronic applications, such as organic semiconductors, thin-film transistors and solar cells [57, 58] as thin-film polarizers [59] as nonlinear optical materials [60], for the detection and amplification of chirality [61, 62] and for separation of enantiomers and enantioselective synthesis [63].

5. Conclusions

Research into the DC phases is in its infancy, but the unique physical and electro-optic properties promises exciting physics and novel applications. There are still many questions to be answered on the exact nature of the structure of these liquid crystal phases, molecular structure-property relationships, role of physical properties such as elastic constants, inter/intra layer interactions on the existence and behaviour of the DC phases. From the point of view of applications, there is a large scope to develop room temperature materials, lower threshold fields and control morphology etc. Overall, from chirality to new electro-optic effects to photovoltaics, the dark conglomerate phases offer abundant scope for chemists, physicists, biologists and engineers to work together for the next generation of liquid crystals' material research and device applications.

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Figure Captions

Figure 1 (a) Representation of primary (**n**) and secondary (**m**) axis on a bent-core molecule, and the rotation of the molecule around the primary axis. (b) Polar smectic A phases; $SmAP_A$, $SmAP_F$ and $SmAP_R$ with antiferroelectric, ferroelectric and random ordering of in-layer polarization between neighbouring layers.

Figure 2 Molecular arrangement in adjacent layers of SmCP phases. (+) and (-) indicates the sign of layer chirality. The combination of tilt direction, layer normal and polarization vector give rise to chirality.

Figure 3 (a) The layer curvature and topography of a sponge phase with empty volume filled with smectic layers. (b) Modulated layers that fill the sponge structure. (c) Deracemized domains of opposite handedness of dark conglomerate phases observed under polarizing optical microscopy.

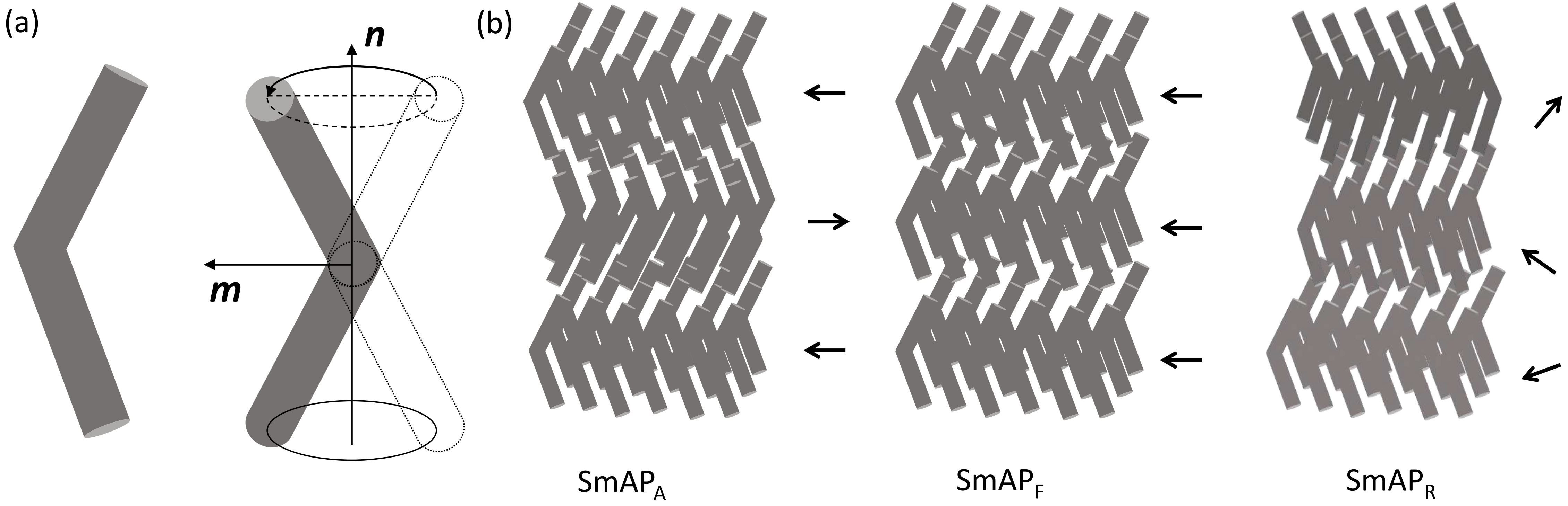
Figure 4 (a) Molecular structure of OC12-Ph-ODBP-Ph-C5 liquid crystal. The transition temperatures are I 230 ^{o}C N167.5 ^{o}C DC 100 ^{o}C Cr. (b-d) POM textures of the nematic to DC phase transition observed under crossed polarizers; (b, c) on cooling (d) on heating. R- rubbing direction. Length of white bar is 100 µm.

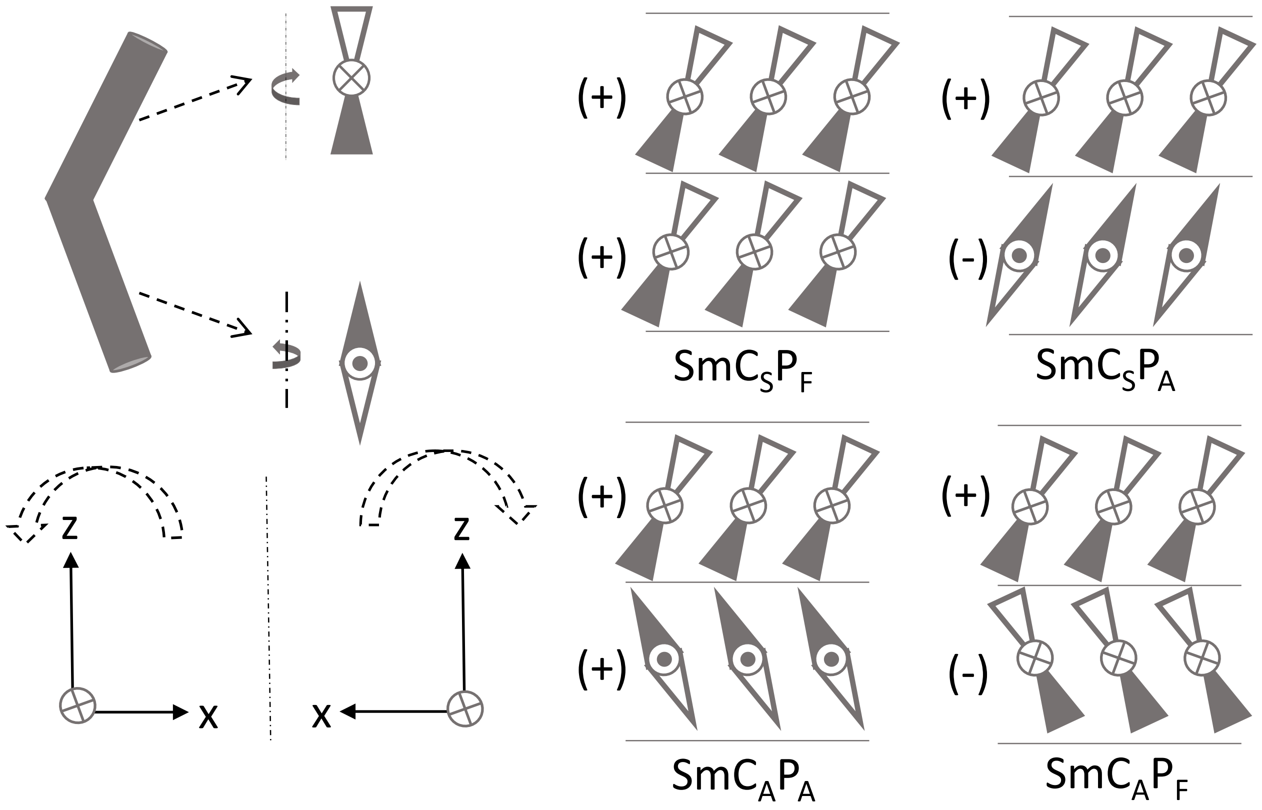
Figure 5 Polarizing optical microscope textures of the DC phase of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal under electric fields. (a,b) at **E** = 8 V/µm, (c, d) at **E**=12 V/µm (e,f) at **E**=14 V/µm. White arrows indicate the polarizer and the analyser directions. Length of white bar is 100 µm.

Figure 6 Plot of (a) layer spacing, d, (b) amplitude, (c) FWHM of the X-ray diffraction pattern as a function of applied electric field in the DC phase of OC12-Ph-ODBP-Ph-C5.

Figure 7 (a) Plot of electric field dependence of dielectric permittivity, ε' and the refractive index, (b) appearance of new peak at 1589 cm^{-1} in the Raman scattering spectra as the electric field is increased, in the DC phase of OC12-Ph-ODBP-Ph-C5.

Figure 8 Diagram of a liquid crystal based microlens. The application of a field induces field-induced focus via the change of the focal power of the liquid crystal layer. R_1 and R_2 are radii of curvature.


(a)
n
m
(b)
SmAP_A
SmAP_F
SmAP_R


z
x
z
x
(+)
(+)
$\mathrm{SmC_SP_F}$
(+)
(-)
$\mathrm{SmC_SP_A}$
(+)
(+)
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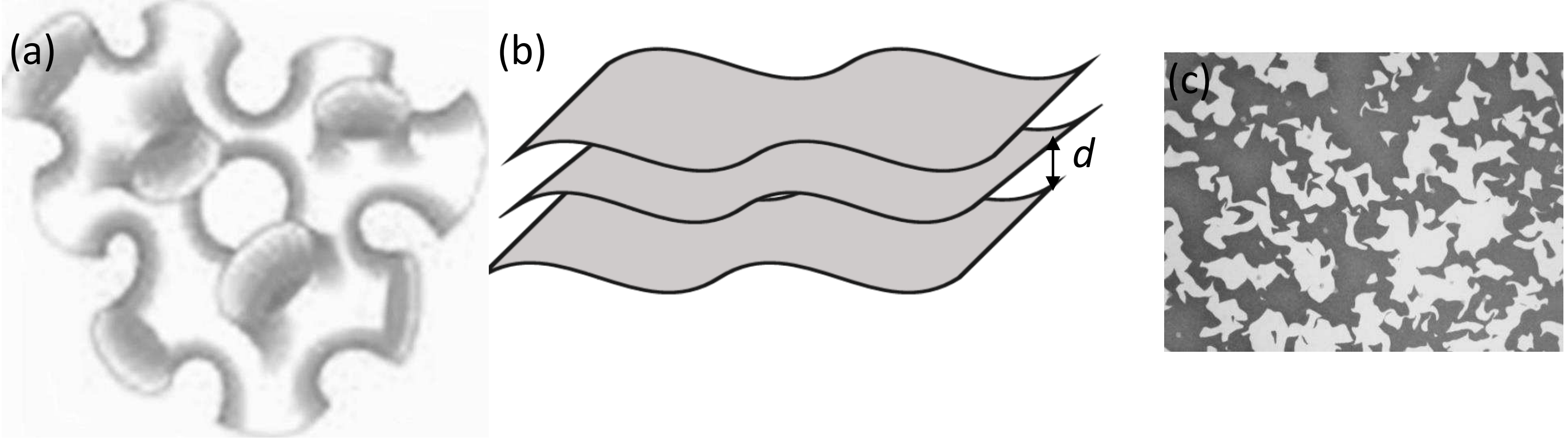
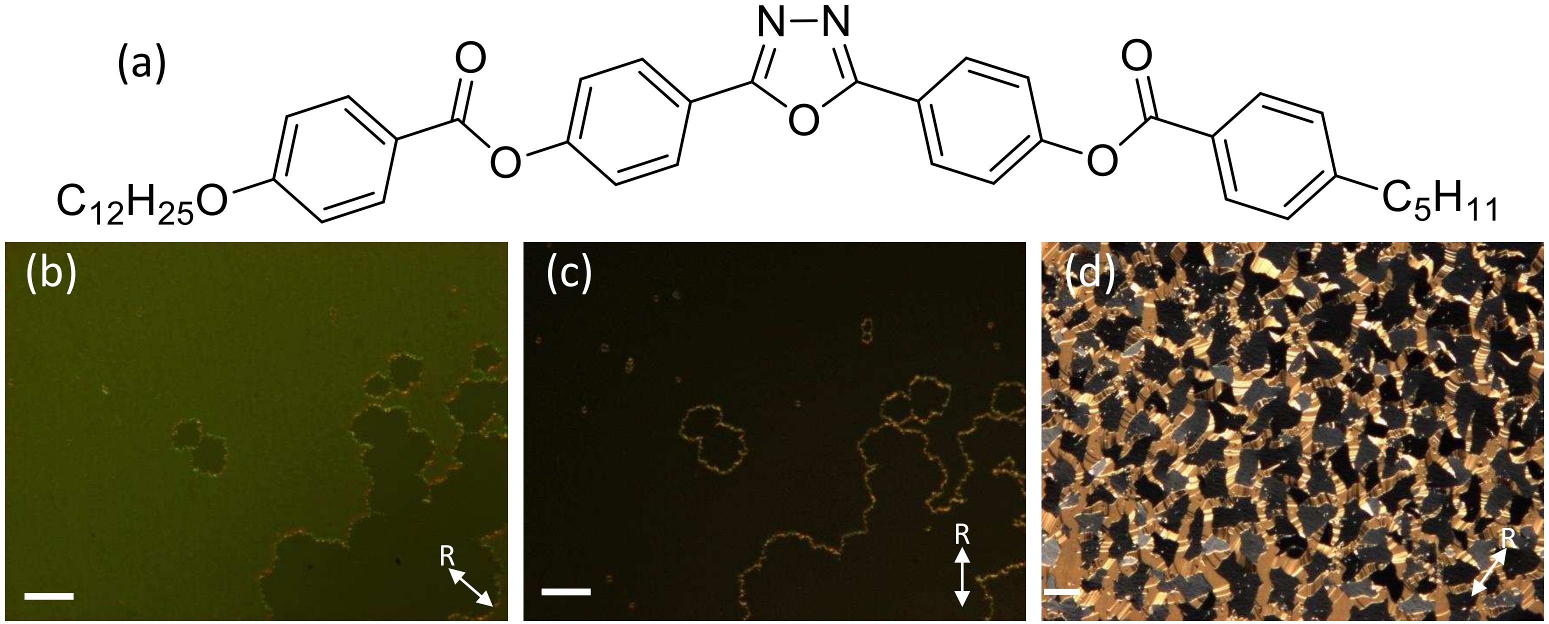
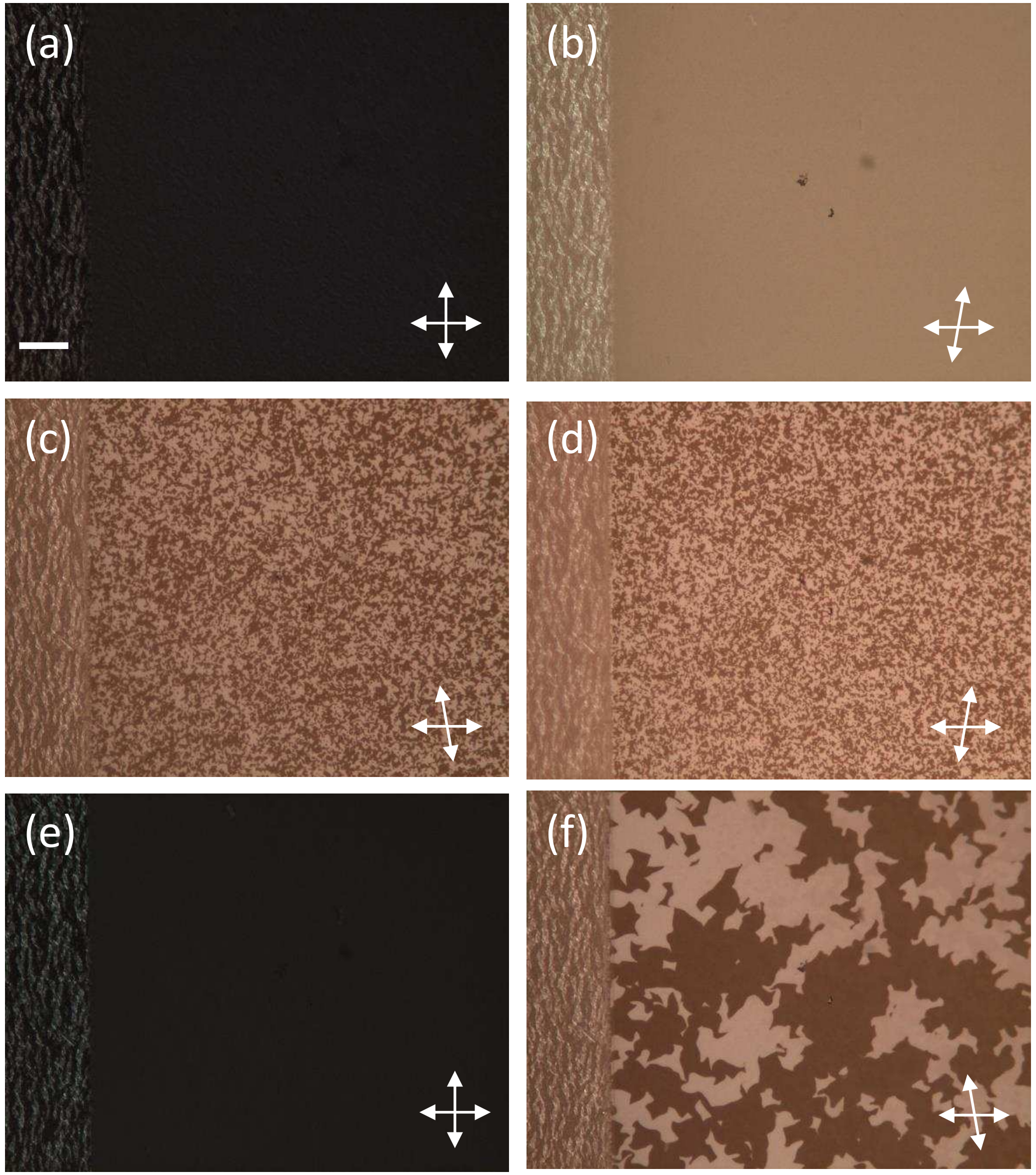
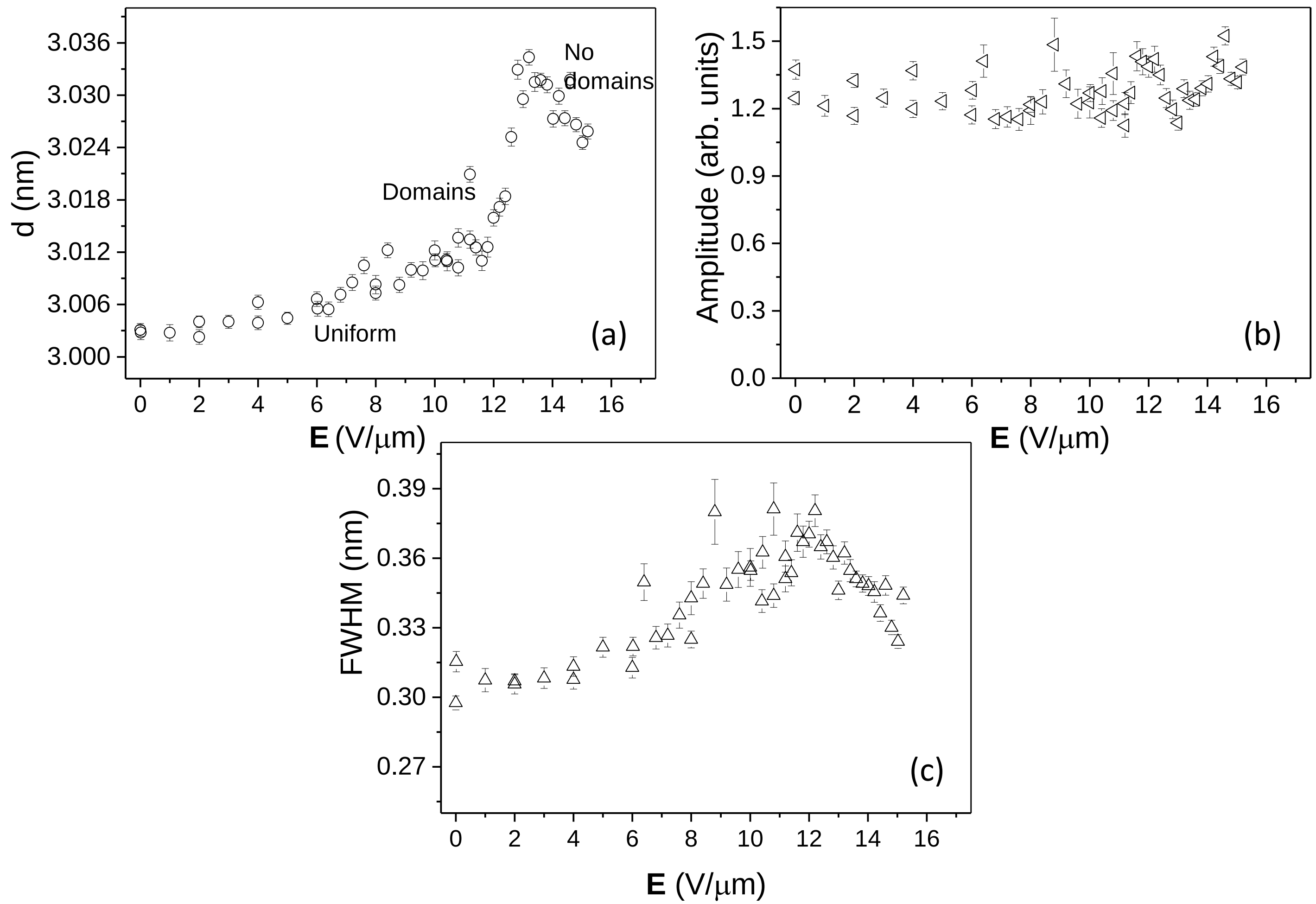
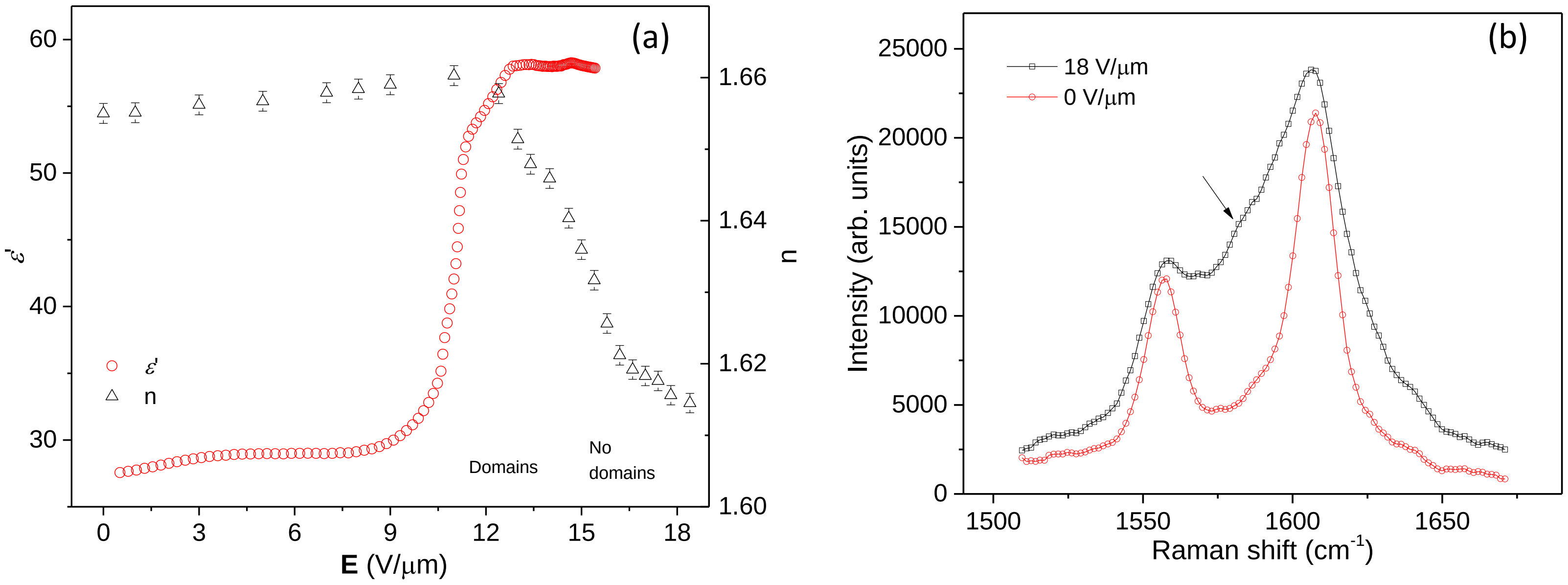
(+)
(-)
$\mathrm{SmC_AP_F}$

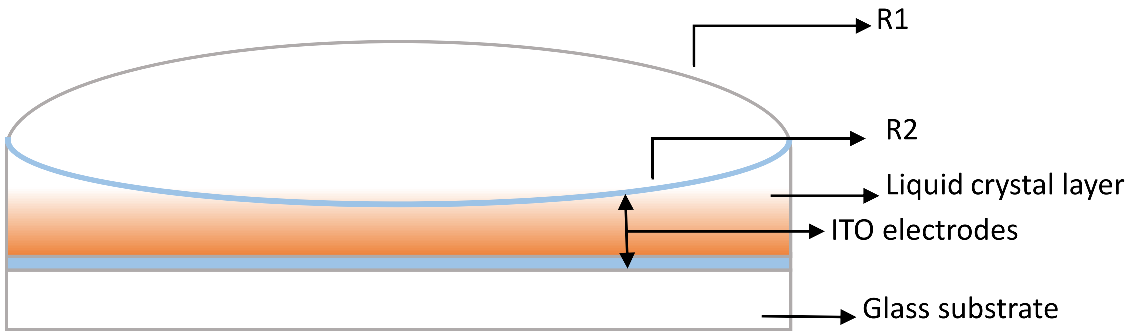

(a)
(b)
d
(c)


(a)
C12H25O
O
N–N
O
C5H11
(b)
(c)
(d)
R
R
R


(a)
(b)
(c)
(d)
(e)
(f)


d (nm)
3.036
3.030
3.024
3.018
3.012
3.006
3.000
No domains
Domains
Uniform
(a)
0 2 4 6 8 10 12 14 16
E (V/μm)
Amplitude (arb. units)
1.5
1.2
0.9
0.6
0.3
0.0
(b)
0 2 4 6 8 10 12 14 16
E (V/μm)
FWHM (nm)
0.39
0.36
0.33
0.30
0.27
(c)
0 2 4 6 8 10 12 14 16
E (V/μm)


(a)
ε'
n
Domains
No domains
E (V/μm)
0
3
6
9
12
15
18
30
40
50
60
1.60
1.62
1.64
1.66
(b)
18 V/μm
0 V/μm
Intensity (arb. units)
Raman shift (cm^{-1})
0
5000
10000
15000
20000
25000
1500
1550
1600
1650


R1
R2
Liquid crystal layer
ITO electrodes
Glass substrate