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Alignment and electro-optical properties of SmC* with direct transition to N* phases

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Abstract

Highly first order silane end-group di-fluoroterphenyl liquid crystal was added to tri-fluoroterphenyl host with a nematic to smectic-C phase transition to increase its first order nature, achieve a higher cone angle and reduce its temperature dependence. Increasing concentration of the additive, caused a linear decrease and eventual disappearance of the nematic phase. A smectic-A phase was injected at 35 % concentration, making the transition second order. Optical studies of the mixtures showed little dependence of the highest value of cone angle on concentration. The original host showed first order cone angle behaviour and was used to fabricate a twisted FLC device.

Introduction

Ferroelectric liquid crystals have the potential to be used as fast electro-optic modulators and optical switches.[1] Our aim is to design novel optical phase modulation devices, which bypass the geometrical restrictions of the smectic A (SmA) phase using designs such as the twisted ferroelectric shutter of reference [1], with microsecond response times for the use in optical beam steering, switchable holographic elements, reconfigurable lenses and other telecommunication applications. These devices require temperature independent smectic C (SmC) cone angles and uniform layer alignment with direct phase transitions from the nematic (N) phase. To maximise the phase modulation, high birefringence materials are used, and a SmC cone angle of 45° was targeted. In this study, mixtures of compounds with direct N - SmC and I - SmC phase sequences were investigated, with the aim of optimising the performance of the fast phase modulators.

When a liquid crystal is cooled into the smectic C phase, the director tilts by an angle θ to the layer normal, known as the cone angle. Decreasing the temperature causes an increase of the cone angle and a concomitant decrease of layer spacing. When placed inside device cells with planar alignment geometry, the layers are effectively confined to the cell walls, so that layer shrinkage results in layer tilt, δ . This creates a chevron interface at the cell centre, where the tilted layers from either cell wall meet. Since the director requires continuity across the depth of the cell, this orients the director at the angle β_0 to the in-plane component of the layer normal. In a system which is cooled from a SmA phase, two types of chevron layer structures, "C1" and "C2", can emerge, depending on whether the layers tilt parallel or antiparallel to the surface pretilt, respectively.[2]. Coexistence of the two chevrons causes disruptive zig-zag defects, but these can be removed through appropriate choices of surface pre-tilts and anchoring strengths.[3] The first order nature of the N-SmC phase transitions, results in a tilt of the layer normal within the plane of the cell.[4] Hypothetically, if the phase transition is strongly first order, neither the cone angle nor the layer spacing change with temperature, and the layers retain this same structure at all

temperatures. In practice, both cone angle and layer spacing do change, and so a chevron structure forms. Usually, only the C1 type of chevron structure is formed, even for cells with a relatively low surface pre-tilt, which can be advantageous for devices such as those with half-V switching.[5]

Introducing chirality to a SmC system, reduces the symmetry of the phase and lets it acquire a ferroelectric spontaneous polarisation, helping ensure faster switching times in comparison to those achieved by dielectric mechanisms due to the strong polar torque induced on the director by the applied field.[6] This torque tends to rotate the director about the cone to align the spontaneous polarisation parallel to the electric field, where the visco-elastic restoring forces balance the ferroelectric torque.

Trifluoroterphenyls are a good example of materials that exhibit wide SmC temperature ranges, direct N to SmC phase transitions and high birefringences (typically $\Delta n \geq 0.2$). [7] In an attempt to increase the cone angle of a chosen trifluoroterphenyl, a silane terminated difluoroterphenyl compound [8] was added at various concentrations, each with 0.5 wt. % of BE80F2N chiral dopant. The aim was to achieve a narrow N* phase to provide a means for good alignment of the SmC* molecules and achieve a more temperature independent cone angle, as silane end-group liquid crystals are known to have highly first order behaviour.

Experimental

The two compounds A and B, shown in Figure 1, were mixed at various concentrations by dissolving the corresponding weights in dichloromethane, sonicating for 30 minutes and evaporating the solvent at 35 °C for 12 hours. Differential scanning calorimetry was used to determine the enthalpy change on cooling into the Smectic C phase for the pure compounds. Compound A has the enthalpy change of 3.34 J/g on cooling through the N – SmC transition, whereas Compound B has the significantly higher enthalpy change of 14.03 J/g on cooling from the Isotropic directly into the SmC phase.

Following mixing, the samples were vacuum filled into home-made glass cells with (5.0 ± 0.2) μm cell gaps and parallel alignment of 1 - 2 ° pre-tilted SE3510 from Nissan. The same components were used for the assembly of a modified twisted device, described in reference [1]. After heating to the isotropic phase on a Linkam T95-PE temperature controller the phase transition temperatures of the resulting mixtures were determined by observing the samples through a polarising microscope on cooling, and checked by DSC.

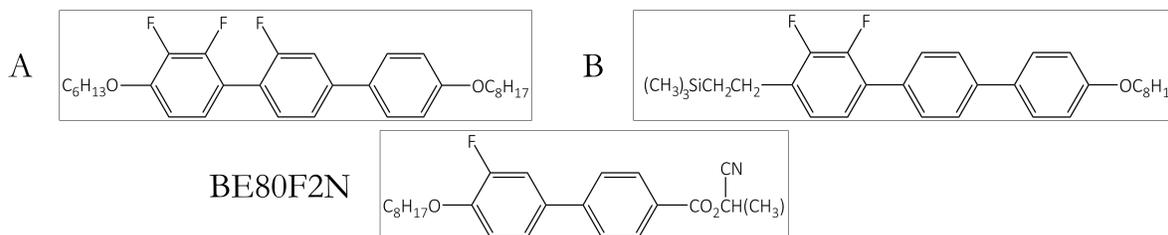


Figure 1 – Chemical structures of (A) 2,2',3-Trifluoro-4-hexyloxy-4''-octyloxyterphenyl [7], (B) 2,3-Difluoro-4-(trimethylsilylethyl)-4''-oxyloxy-[4,4':1',4'']-terphenyl [8] liquid crystals and BE80F2N chiral dopant.

Using the same procedure, BE80F2N (chiral dopant) was added at 0.5 wt. % to the selected compounds (indicated by *) to induce a small amount of spontaneous polarisation (2.0 ± 0.1 nC/cm² at 10 °C below

the N*-SmC* phase transition for compound A) and enable ferroelectric switching. A small amount was chosen to avoid significant changes of the phase transitions and the cone angles of the mixtures. Following this, the samples were capillary filled in glass cells with 1.8 μm cell gaps in the isotropic phase. Each cell had planar alignment layers with 1° parallel pre-tilt and 10 Ω/\square indium tin oxide electrodes. Due to the low cell gap, the pitch of the N* was unwound completely, which allowed good layer formation in the SmC* phase. To measure optical properties, square waveforms with amplitudes ranging from 0 V to 10 V were applied across the samples at a frequency of 0.1 Hz. Applying the electric field switched the spontaneous polarisation vector, which points tangentially to the base of the cone, around the layer normal. For a given temperature in the SmC* phase, optical extinction angles were measured for each voltage on both sides of the layer normal. A linear dependence of the extinction angles on the inverse of the applied voltage was assumed to find the corresponding asymptotes for different temperatures. This gave the in-plane direction of the layer normal, α , and the infinite field extinction angles, β_∞ . For known β_0 and β_∞ , trigonometric consideration of overlapping cones at the chevron interface yields the following equation

$$\cos \delta = \frac{\cos \theta}{\cos \beta_0} = \frac{\tan \theta}{\tan \beta_\infty}, \quad (1)$$

which can be evaluated to give θ and δ . [9]

Phase transitions

The phase diagram in Figure 2 shows the transition temperatures of seven liquid crystal mixtures of A and B. Compound A exhibits a N - SmC phase transition at 125.5 °C, while compound B has a direct transition From I to SmC at 142.8 °C. There is a 3 °C dip in the isotropic to liquid crystal phase transition curve for the intermediate concentration range, suggesting imperfect miscibility. The nematic to smectic phase transition temperature shows a linear increase with increasing B content. Eventually, the nematic phase completely vanishes near the 50:50 concentration. Furthermore, a narrow band of SmA was introduced at 65:35 and 60:40 concentrations. These concentrations remove the direct N - SmC phase transition and make the transition to SmC second order. The dotted line in the phase diagram shows a linear approximation to the point at which the induced SmA phase vanishes, which crosses the I - SmC transition curve. This indicates that compound B has some SmA tendency, which causes the injected phase, despite showing a strongly first order I - SmC transition..

It did not prove possible to increase the first order nature of the N-SmC in the mixtures, as shown by the measured enthalpies in the bottom part of Figure 2. Rather than increasing the enthalpy across the phase diagram as the width of the nematic phase is reduced, and the content of the silane terminated compound increased. Indeed, the addition of the silane end group gives a discontinuous jump at the concentration where the transition from the SmC is direct to the Isotropic. Nevertheless, comparing the optical angle measurements of the 60:40 mixture, C, to those for A draws a perspective to the amount by which the cone angle can change for the other mixtures that show the desired N - SmC phase transition.

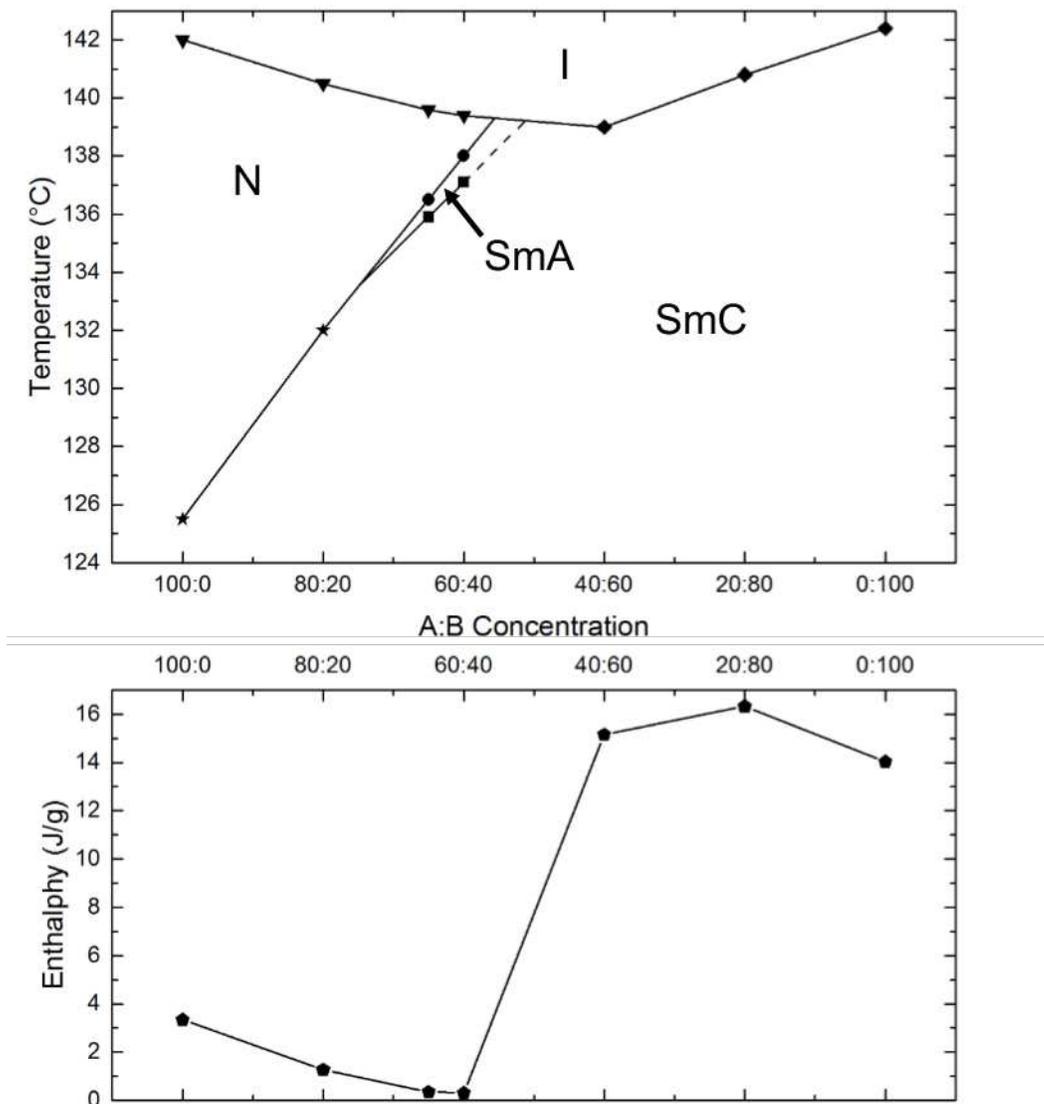


Figure 2 – Top: Phase diagram showing phase transition temperatures of mixtures of A and B as a function of concentration. Bottom: Corresponding enthalpy changes upon entry into the SmC phase on cooling, measured using a DSC. Lines connecting symbols are linear approximations and guides to the eye only.

Alignment

When observed in a planar cell, it was found that compound A* experiences a first order cone angle increase at the N* - SmC* phase transition, shown in Figure 3. At 0.1 °C below N* - SmC* phase transition, T_{NI} , θ was found to be $(19.9 \pm 0.1)^\circ$ and then increased to $(30.9 \pm 0.6)^\circ$ when it was cooled to 20.0 °C below T_{NI} . At the transition, the formation of layers also showed first order behavior. At 0.1 °C below T_{NC} , the layers experienced an in plane layer azimuthal angle, α , of $(18.1 \pm 0.1)^\circ$ and an out of plane layer tilt, δ , of $(8.5 \pm 1.0)^\circ$. After further cooling, α had a small increase within a few °C and remained at a constant value of around 20°, while δ kept gradually increasing to $(17.0 \pm 2.0)^\circ$ over the 20 °C temperature range. For this compound the value of δ/θ ranges from 0.4 to 0.6, with decreasing temperature. Further cooling resulted in the formation of defects associated with the mismatch between

the surfaces and the shrinking layers, which made the extinction angles hard to distinguish. Figure 4 shows the temperature dependence of θ , α and δ for compound A*. It also shows a fitted curve for the cone angle, which follows the relationship:

$$\theta = \theta_0(T_{NC} - T)^\gamma + \theta_1, \quad (2)$$

where T is the temperature and θ_0 , θ_1 and γ are fitting parameters. Fitting the data gave $\theta_0 = (12.5 \pm 1.2)^\circ$, $\gamma = (0.15 \pm 0.01)^\circ$ and $\theta_1 = (11.1 \pm 1.2)^\circ$, which is highly sensitive near T_{NC} due to a higher gradient of θ in that region.

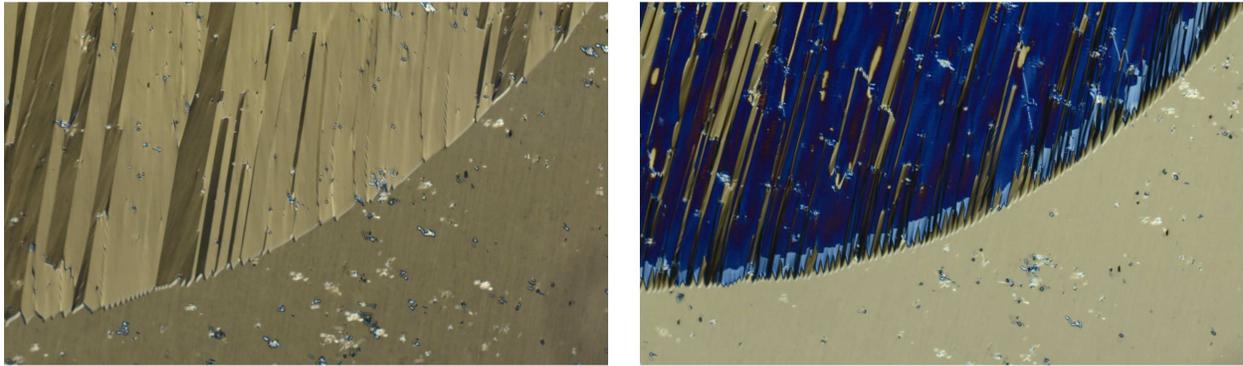


Figure 3 – Photographs showing the N* (bottom) - SmC* (top) phase transition of compound A, with no applied voltage (left) and 2.5 V (right). Width of each image corresponds to 600 μm .

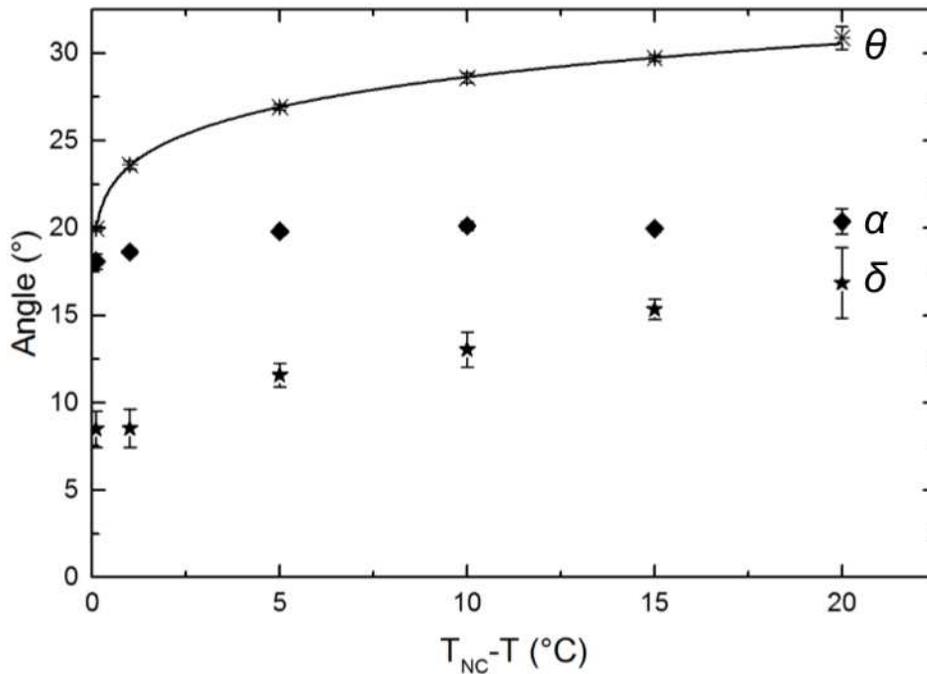


Figure 4 – Temperature dependence of the cone angle, θ , layer tilt, δ , and in-plane layer twist, α , for A*.

The layer tilt deviates considerably to that anticipated for materials with the N-SmC phase sequence. In the nematic phase, the director has a slight bend-splay due to the 1° pre-tilt, but is otherwise uniformly aligned. At the first order transition to the SmC phase, the cone angle forms at θ_1 (i.e. much higher than 0), which would be expected for a second order transition. Therefore, at the transition, the layers may form at this angle to the nematic director (i.e. the rubbing direction) and be between the limiting cases of $\delta = \theta_1$ and $\alpha = 0$ or $\delta = 0$ and $\alpha = \theta_1$ and is given by

$$\cos \theta_1 = \cos \delta \cos \alpha, \quad (3)$$

which can be shown by simple trigonometrical arguments. Considering the data obtained at 0.1 °C below T_{NC} , (3) results in $\theta_1 = (19.9 \pm 0.5)^\circ$, which has the same value as the measured θ . Since the cone angle increases but α remains constant at lower temperatures, this relationship is only valid very close to the transition temperature.

Figure 5 shows the temperature dependence of the cone angle θ and the layer tilt angle δ calculated from the electro-optic results for mixture C*. This mixture showed smaller features than A* and a much greater number of defects that appeared quickly, making the measurements less accurate. Since this compound had an injected SmA phase, the transition to SmC* was second order and there was no in-plane layer tilt (i.e. $\alpha = 0^\circ$) and both θ and δ started from zero at the phase transition. Cooling to 1.5 °C below T_{AC} resulted in a rapid increase of θ and δ to $(16.9 \pm 0.3)^\circ$ and $(15.8 \pm 0.3)^\circ$, respectively. Cooling by 15 °C increased θ to $(29.8 \pm 0.5)^\circ$ and δ to $(26.2 \pm 2.0)^\circ$. As before, Figure 5 also shows a fitted curve of θ , where $\theta_0 = (18.3 \pm 0.2)^\circ$, $\gamma = (0.16 \pm 0.01)^\circ$ and $\theta_1 = 0^\circ$. This shows that the cone angle of C* grows to a value that closely matches that of A*, within the experimental error. In contrast to A*, δ/θ is in the range of 0.85 - 0.95, which is typical for SmA - SmC liquid crystals.[2] This suggests that mixing A and B does not result in a higher cone angle with a lower temperature dependence.

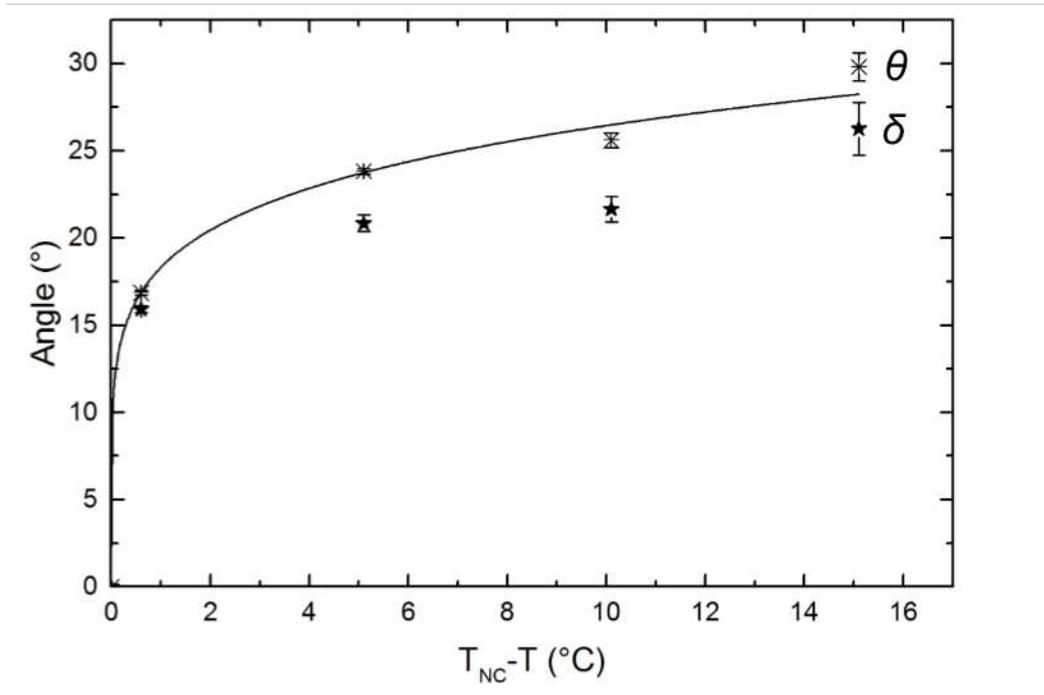


Figure 5 – Temperature dependence of the cone angle, θ , and layer tilt, δ , α , for C*.

Twisted Device

Despite the failure to increase the cone angle to 45° through mixing, compound A* had a first order increase to 20° as it was cooled from N* to SmC*. This was placed in a device with a $(3.1 \pm 0.3) \mu\text{m}$ cell gap and a 40° twist of planar alignment directions. At 0.1°C below T_{NC} , the device showed a smooth single domain across the cell. Applying a DC voltage across the cell resulted in reorientation of the director and phase modulation. Figure 6 illustrates the basic concepts the design of this device and the effects of applying 5 V at this temperature. Cooling down further resulted in a swift appearance of defects due to layer shrinkage and the growth of the cone angle, making the device unusable after a couple of $^\circ\text{C}$. This shows that phase modulation in SmC* twisted devices can be achieved for materials with cone angles lower than 45° , as described in reference [1], but requires them to be temperature independent.

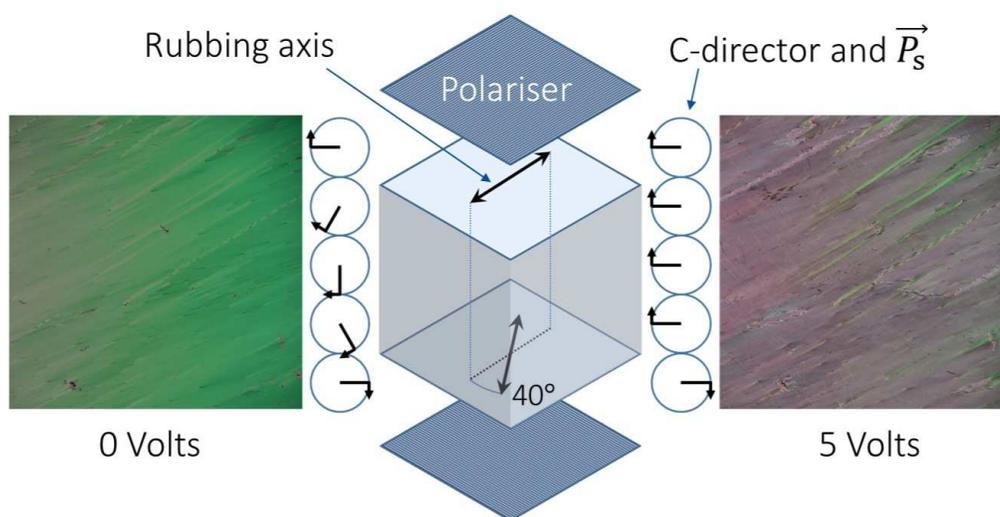


Figure 6 – Compound A* in a $3.1 \mu\text{m}$ cell with 40° planar aligned surfaces at 0.1°C below T_{NC} showing phase modulation between 0 V and 5 V states. Width of each image corresponds to $500 \mu\text{m}$.

Conclusion

Mixing two terphenyl liquid crystals with direct N - SmC (A) and I - SmC (B) phase transitions resulted in a linear decrease of the width of the nematic phase, which vanished near the 55:45 concentration of the two. Between 80:20 and 65:35 concentrations a narrow SmA phase was observed. The cone angle of A showed first order behavior at the N - SmC phase transition, while that of the 60:40 mixture followed the typical second order SmA - SmC behavior. Both reached a value of 30° within 15°C of the phase transition upon cooling, which suggests that the cone angle does not have a noticeable change for mixtures of A and B with a nematic phase, which is necessary for good alignment. Compound A was used in a device with a 40° twist in the SmC*, which had uniform alignment and showed phase modulation with applied electric fields. However, it was found that the structure is easily disturbed by changes in the cone angle and therefore temperature. Future studies will investigate compound A for various applications which require a direct N - SmC phase transition.

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