On the effect of carbon nanotubes on properties of liquid crystals

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Liquid crystals (LCs), with their fluidity and self-organization, are attractive hosts for the dispersion and manipulation of macro- and nanoparticles, allowing the realization of their ordered assemblies. In addition, new functional materials can be created owing to the particle properties. Among the nanoparticles, carbon nanotubes (CNTs) stand out for their exceptional electrical, thermal and mechanical properties. While LCs can be used for manipulating CNTs, the nanotube properties are attractive also for influencing and tuning LC properties. In this paper, we discuss different aspects of the CNT–LC combination, briefly introducing their dispersion and interaction and then, more extensively, evaluating the CNT effect on selected properties of LCs relevant to display-related applications. We show that some previously reported improvements cannot be considered an intrinsic feature of CNT-doped LCs. In addition, we are also able to follow locally the Frederiks transition of CNT-doped LCs by Raman spectroscopy, revealing the direct effect of bundles of CNTs on LC reorientation.

1. Introduction

Liquid crystals (LCs) and carbon nanotubes (CNTs) form an intriguing combination of hard and soft matter with anisotropic properties [1–4]. CNT–LC composites have attracted attention in display applications, as discussed later, but also for the possibilities to disperse and, at the same time, organize CNTs. The latter is...
an attractive possibility, with LCs acting as templating medium, either for ordering CNTs, after host removal, or in composites [3,4].

CNTs are formed by a layer of carbon atoms arranged in a honey-comb fashion (graphene) that rolls up, creating seamless cylinders [5]. Since their diameter is in the nanometre range, although their length is orders of magnitude larger, CNTs belong to the category of nanoparticles. The aspect ratio of CNTs is outstanding since their length can range between hundreds of nanometres to the order of millimetres. The properties of CNTs are also remarkable, exhibiting very high electrical and thermal conductivity and possessing exceptional mechanical properties [6]. They can be electrically metallic or semiconductive with, in addition, different possible values of the band gaps, depending on the way the graphene sheet is rolled up, indicated by the so-called chiral indices (n, m) that allow the identification of the tube properties. Despite their attractive properties, the use of CNTs presents several challenges connected to the variety of properties of the as-grown tubes and difficulties in their manipulation and control of their organization.

A critical issue for the handling and application of CNTs is their tendency to form entangled aggregates. Aggregation is detrimental for several reasons and in applications of both bare and composite CNTs. For example, CNTs show a very low electrical percolation threshold because of their very high anisotropy in shape, but this threshold is strongly reduced if the nanotubes aggregate. Also in composites, if the distribution of CNTs in a material is not uniform, the transfer of the desired properties from CNTs to the host is not satisfactory. Even in nanoelectronics, only isolated or very small bundles are desirable for optimum performance.

Aggregates induce disorder in the orientation of nanotubes, randomizing their alignment and thus averaging out their anisotropic properties. This disorder has a great contribution in the lack of transfer of the properties measured on a single tube onto the macroscopic world. The overall properties are strongly reduced compared with the high performance values expected from single tube measurements. Therefore, ordering the CNTs allows one to enhance the macroscopic properties, either in composites or of ensembles of CNTs, e.g. transistors. Different manipulation methods have been explored to organize CNTs and, among those, LCs have been successfully used, allowing unidirectional ordering of CNTs via the formation of LC phases of nanotubes [7–10] or by transfer of order from the LC host onto embedded CNTs [11–16]. Thus, LCs, unlike ordinary fluids, can disperse particles and, at the same time, manipulate them. This has been demonstrated for thermotropic as well as lyotropic LCs [3]. Among thermotropics, different types of hosts have been used [17–19], finding some very intriguing effects such as chirality transfer [17].

CNTs can be formed by a single graphene wall (SWCNTs), as recognizable in figure 1a, or by multiple concentric walls, the multi-wall CNTs (MWCNTs), in figure 1b. The latter have, in general, a lower aspect ratio than SWCNTs owing to the larger diameter resulting from the concentric walls that can range from two to tens or even hundreds of walls. The CNT dimensions can also change according to their synthesis methods and growth parameters. The
growth conditions also affect the occurrence of defects and the presence of by-products such as amorphous or other forms of structured carbon or metal catalysts. Optimization of the growth processes, post-growth purification and fractionation techniques have brought huge progress in the selection and quality of available CNTs. However, more advances are still required in order to achieve a perfect control of size, type and quality of CNTs and, thus, of the desired properties useful in specific applications, including displays.

While both classes of LCs, thermotropics as well as lyotropics, can disperse and align CNTs, the ease of dispersion, the achievement of large-scale, uniform alignment and the possibility of dynamic control of the CNT orientation present differences for the two classes. In this article, we focus on the thermotropic hosts, briefly discussing known problems in dispersion, and presenting our work on the effect of CNT doping on properties of LCs that are potentially interesting for display applications.

2. Dispersion and interaction

CNTs are notorious for the difficulties in dispersing them owing to the very strong van der Waals forces keeping the tubes strongly together. As particles reduce their dimension, the effect of surfaces becomes more and more important compared with the contribution of the volume. Dimension is also important in Brownian motion in colloidal suspensions, making it a relevant process for nanoparticles, inducing an increase in the collision rate. Owing to the van der Waals forces between nanoparticles, collisions then generate aggregation. This makes it difficult to produce mono-disperse, stable nanoparticle suspensions.

CNTs already bundle during growth and even when they are debundled by mechanical means, they tend to re-bundle. It is expected that the van der Waals forces for CNTs are so strong because of the reduced dimensions, but also because of their strongly anisotropic shape. Thus, CNTs form ordered bundles, which in turn form disordered aggregates. A real solvent for their dissolution does not exist. For breaking up the bundles, ultrasonication is typically employed since strong forces are needed to overcome the tube–tube attraction. In order to prevent re-aggregation, one of the standard approaches in the case of aqueous dispersions is the use of surfactant molecules that would coat the nanotubes and, by steric or electrostatic action, keep the tubes apart. Other approaches, still based on non-covalent methods, use some organic solvents, polymer or superacid treatments. Alternatively, researchers have developed covalent functionalization routes that can make CNTs soluble even in water owing to covalently bonded groups, although at the expense of deteriorating the CNT properties.

While lyotropic LCs, formed by surfactant molecules, can be used for efficiently dispersing CNTs, profiting of the existing knowledge in the field of surfactant-based CNT dispersions and, at the same time, organizing the nanotubes [16,17], dispersion in thermotropics has different challenges. The typically used surfactant molecules, formed by a hydrophobic part, which tends to adsorb on the nanotube surface since CNTs are hydrophobic, and a hydrophilic part, pointing towards the aqueous medium, are not compatible with the thermotropic hosts, as they are non-polar. This means that surfactants are not useful for dispersion of CNTs in thermotropics. Thus, new strategies and studies have to be specifically devoted to thermotropics [21]. The work performed so far has shown that thermotropic LCs exhibit peculiar features in dispersion of CNTs. The first moments of dispersion of CNTs in different LC hosts with ultrasonication are surprisingly efficient, for all studied LCs, in obtaining a fast, coarse CNT suspension, comparable to the best organic solvents. However, at a later stage, the molecular structure and composition of the LC appear to have a key role, delivering quite different results in terms of final dispersion quality [22].

The molecular structure is not the only factor entering into an optimal dispersion process. Isotropic LC phase transitions and the use of an LC host with too low transition temperatures have to be avoided. This aspect is quite relevant considering that, as for isotropic hosts, powerful sonication is needed to break up the aggregates and the local temperature can therefore rise considerably during the debundling, thus inducing isotropization of the host. Interestingly, the
LC phase *per se* is beneficial for CNTs, providing improved dispersion compared with the results obtained for the same host but in the isotropic phase. The phase transition is detrimental to the stability of the CNT dispersion, inducing aggregation, because of phase segregation occurring when the LC domains start to form. The CNTs are then expelled into the isotropic areas. However, the isotropic phase seems also less favourable compared with dispersions prepared totally in the LC phase. In fact, sediments and larger aggregates are more easily formed in the isotropic phase compared with the LC phase. The anisotropic diffusion coefficients and/or the reduced thermal motion can probably contribute to the difference in performance, which makes LCs interesting and unusual hosts for CNT dispersion.

In summary, the molecular structure of thermotropic LC hosts can strongly influence dispersion, presumably because of differences in the interaction strength between CNT surfaces and LC molecules. If the surface interaction is very weak, the host is expected not to be favourable in sufficiently counteracting the CNT aggregation. It is worth stressing that even in the presence of strong anchoring, this mechanism alone cannot be comparable with the electrostatic repulsion provided by the surfactant molecules. Thus, the CNT concentration that can be accommodated in thermotropics before generating bundles is generally orders of magnitude lower than in lyotropics.

However, if the molecules are able to ‘stick’ on the CNT surface, then the CNT re-aggregation can be hindered, or ‘soft’ bundles can be formed, with tubes close to each other but not tightly aggregated and easy to debundle.

An ideal dispersion of CNTs in thermotropics for display applications has no or very small CNT bundles. In fact, if CNTs are single dispersed, they do not perturb the LC alignment and therefore do not induce director distortions detrimental to display applications. We have taken advantage of the acquired knowledge for dispersion in thermotropics for the preparation of CNT suspensions used in the experiments presented in §3.

3. Effect on display properties

LCs are the dominant material in modern display technology. Nevertheless, the quest for better performing displays drives research towards looking for faster switching, lower switching threshold voltages, higher contrast ratios and so on. Since nanoparticles have reduced dimensions, relevant for minimizing director distortions, and generally show enhanced electrical and mechanical properties, they have attracted much attention in the last few years in combination with LCs for new electro-optic effects, such as a change in the plasmonic frequency of gold nanoparticles but also for improving display-related properties, increasing dielectric anisotropy, decreasing rotational viscosity and similar features. Commercial compounds are already performing quite well, but improvements are still needed for facing new technological trends. Among the different nanoparticles, CNTs have been explored because of their extremely anisometric shape and exceptional anisotropic properties, making them powerful dopants for adjusting the anisotropic properties of LCs. Earlier reports have been presented suggesting that doping nematic LCs with CNTs can enhance their electro-optic properties for use in display devices. Reports include a CNT-induced decrease of the Frederiks threshold (the threshold for switching the director orientation between the surface-induced OFF state and the field-induced ON state) [23–28], suppression of ionic field screening [24,27,29–31] and increased switching speed [23,26,28]. The situation is however confused by data showing the opposite behaviour: unaffected or even clearly increased switching threshold [25,26,28–31], clear signs of increased ion content [26,31] and slower switching [25,26,28]. While it is difficult to understand the origin of the discrepancy between the different reported results, due to lack of information on CNT quality, preparation procedure or crucial aspects of the experimental conditions, there are indications that the CNT concentration plays an important role [26] but also dispersion quality.

The switching time of LCs depends on their dielectric anisotropy. The higher the anisotropy of the LC, the faster the switching. Thus, it is attractive to add anisotropic particles that can contribute to increasing the LC dielectric anisotropy. CNTs can be electrically conductive or
semiconductive and they possess an extremely high aspect ratio. Thus, their dielectric anisotropy is extremely high, but is different between metallic and semiconducting CNTs [32]. The high value of the dielectric anisotropy is expected to be able to contribute strongly to the increase in the dielectric anisotropy of an LC host. CNTs can reorient under the application of external electric or magnetic fields. If this reorientation occurs at a voltage value smaller than the one for LCs, then the reorientation process can be improved. This reasoning was proposed early on by Brochard and de Gennes [33] for LC reorientation by magnetic fields.

The typical concentration of CNTs, used as dopants in display-related work, is quite low to avoid short circuits, occurrence of unwanted change in LC properties or distortions of the director. The present study starts with the evaluation of the dielectric properties of LCs doped with CNTs, at low CNT concentration as in typical work for displays and for which dispersion quality appears satisfactory. Different types of CNTs have been considered in this work since the type, single- or multi-wall, and also the growth methods and purity can influence the result of the experiments. The dimensions, the presence of defects, purity and the distribution of species with specific chiral indices (n,m) can strongly vary according to the CNT production method. This variety has an impact on the properties of the investigated CNTs and has an even greater importance when CNTs are used for doping LCs at minute quantities.

We have used different types of CNTs: as-grown SWCNTs and MWCNTs produced by laser ablation (LA SW) and arc discharge (AD MW) methods, respectively, super-purified high-pressure carbon monoxide (HiPco) SWCNTs (HiPco SW), purchased from Carbon Nanotechnologies Incorporated, with a nominal purity of less than 5 wt% ash content and MWCNTs produced by Nanocyl (NC MW) by chemical vapour deposition. As impurities, one can expect metal catalyst rests, amorphous carbon and non-tubular fullerenic carbon structures, which are by-products of all growth methods, except for the MWCNTs produced by arc discharge, for which no metal catalysts were used.

The LC hosts were the cyanobiphenyl-based four-component mixture E7 from Merck, and the mixture ROTN-403 (abbreviated to RO in the following) from Hoffmann-La Roche, exhibiting positive dielectric anisotropy and a broad temperature range of the nematic phase, including room temperature.

After weighing out the dry CNTs in a vial, this was filled with an amount of LC, giving the resulting mixture a CNT concentration of 0.01% by weight. The CNTs were dispersed in the LC using low-power sonication by placing the sample in a sonication water bath (Branson 200, 19 W at 40 kHz). Strong sonication, although effective in debundling CNTs, can induce defects in the nanotube walls, which we want to avoid in order to preserve the pristine properties. Thus, special care was taken in dispersing the nanotubes as gently as possible when using ultrasound.

The samples were centrifuged and decanted prior to filling into cells, otherwise, optically visible bundles were always present. As this process resulted in an uncontrolled reduction in CNT content, the concentrations stated above should be understood as generous upper limits of the real concentrations.

For the dielectric spectroscopy investigations (carried out at a temperature of 30°C using an HP4192A impedance analyzer), the mixtures were filled into 10µm thick LC sample cells with transparent indium tin oxide (ITO) electrodes. The cells have rubbed polyimide layers for planar alignment of the LC in the field-free state.

We focus not only on the value of the Frederiks threshold after doping with CNTs, but also on the dielectric anisotropy of the composite and on the consequences on ions. The effect on the Frederiks threshold was tested by measuring the dielectric spectrum of each mixture as a function of an applied DC bias field, increasing in small steps from 0 to 15 V. Each frequency scan with a positive bias was followed by an identical scan with a negative bias in order to minimize the effects of long-term DC field application. Throughout the experiments, the polarizing microscopy sample texture was automatically monitored. Below the threshold, the measured real dielectric permittivity $\varepsilon'$ is the smaller $\varepsilon'_{\perp}$ value, reflecting the planar-aligned ground state, while above the threshold, $\varepsilon'$ increases up towards the maximum value $\varepsilon'_{\parallel}$, measured in homeotropic alignment (director perpendicular to the cell plane). Figure 2 shows $\varepsilon'$ at a representative frequency as a
Figure 2. The real component of the dielectric permittivity at a frequency of 10 kHz as a function of the applied bias voltage for the two LCs studied, with and without CNT dopants.

function of DC bias for the two LC mixtures, pure and doped with CNTs, and for E7 with different types of CNTs. As can be clearly seen, the only effect of adding CNTs found in this study is adverse, the threshold generally occurring at slightly higher DC voltage in the doped mixtures. The increase is quite strong in the case of HiPco-doped RO, while the threshold of the E7 host is less affected. An analysis of the textures observed during the experiment fully supports the conclusions from the dielectric data.

The actual content of nanotubes is different between the purified and unpurified samples, but this does not have noticeable consequences on the observed trend. Interestingly, the smallest change in the switching threshold was observed when doping with one of the non-purified samples (AD MWCNTs). We believe that dispersion of the CNT sample in the LC with subsequent centrifugation and decantation actually brings about a certain degree of purification, with the larger impurities being sedimented at the bottom of the vial during centrifugation and thereby being removed from the sample to be studied. This, together with the fact that no catalyst particles are introduced with the AD sample, may explain why these CNTs had no adverse effects on the LC.

The dielectric anisotropy $\Delta \varepsilon'$ for the samples was calculated by subtracting $\varepsilon'$ at the maximum DC bias from the corresponding value in the bias-free ground state. The resulting $\Delta \varepsilon'$ at a frequency of 10 kHz is shown in figure 3a for all mixtures investigated. Very small differences between the doped and undoped LC were detected, below experimental error. We can thus confirm no change to the dielectric anisotropy induced by CNT doping, at the concentrations used in this work.

The above results may lead to the suspicion that some samples actually did not contain any CNTs. However, the presence of nanotubes was easily confirmed by studying the conductivity of the samples for the case of LCs with and without CNT dopants, as well as by Raman spectroscopy. These data will be shown elsewhere.

For assessing the effect of CNTs on the ion content, we studied the low-frequency regime of the real component of the dielectric permittivity $\varepsilon'$ of the virgin cells, without any DC bias applied; cf. Figure 3b. The presence of ions in the sample leads to a so-called ‘electrode polarization’ contribution to $\varepsilon'$ at low frequencies [34]. If the effective ionic content is changed by CNT doping, the low-frequency permittivity should thus change as well, decreasing in the case of a desired reduced ion content. However, we could not find any noticeable reduction in $\varepsilon'$ in either LC host.
We saw a slight increase in the case of HiPco-doped E7, suggesting that ions in this case could have been introduced with the SWCNT sample. No change was detected when the same type of CNT was added to the other LC host. We can suggest a difference in the final CNT concentration as a possible reason for the different effect of HiPco on the two hosts. Differences can be observed after centrifugation because of the different affinities of diverse LC hosts with CNTs. Although there was no clear difference in the concentrations in the two hosts, we could expect a slightly lower amount of remaining CNTs in the RO sample than in the E7 sample. This is because CNT suspensions in the latter LC were found by Schymura et al. [22] to survive centrifugation much better than suspensions prepared using RO.

4. Reorientational threshold and carbon nanotube bundles

As previously mentioned, CNTs tend to form aggregates that are detrimental to their manipulation and applications. They are also undesirable in LCs since they can induce short circuits in electro-optic experiments and director distortions. Even if the size of the bundles is not big enough to create short circuits, they are still not beneficial for LC applications. Here, we demonstrate the importance of having high-quality dispersion with debundled CNTs by showing a substantial change of the LC reorientational threshold in the presence of very large CNT bundles. The previous investigations, based on dielectric spectroscopy, give an average behaviour since the measurement probes the CNT–LC properties in an area defined by the dimensions of the ITO electrodes. These types of investigation are very relevant for displays and for obtaining general trends, but cannot give a direct relation between the presence of CNT aggregates and LC behaviour. The quality of the dispersion can also have a strong, adverse effect on the display properties.
Figure 4. An extract of the Raman spectrum of the E7 LC in an ordinary cell. The peaks from the aromatic ring and the cyano group stretching modes are clearly distinguishable. The peaks are located at 1608.5 cm$^{-1}$ and at 2229.4 cm$^{-1}$, respectively.

We have studied the switching response of LCs by locally probing the reorientational threshold using micro-Raman polarizing spectroscopy. In this way, we follow the LC reorientation just at the desired location, in the area defined by the beam spot. Raman spectroscopy experiments were carried out using a Jobin Yvon Labram Raman microscope in the back-scattering mode, with a 632.8 nm wavelength excitation laser. A lambda half plate was used for controlling the polarization of the input beam, and a regular polarizer was employed for analysing the output beam. The Raman spectrum was acquired from low wavenumbers up to 3000 cm$^{-1}$. In figure 4, the most pronounced peaks in E7 are shown. On the far right, the stretching mode of the cyano group at 2229.4 cm$^{-1}$ and, in the middle, the one from the aromatic rings at about 1608.5 cm$^{-1}$ are visible. These modes can be used for probing the LC alignment and measuring the order parameter since their intensity is orientation dependent, and is highest for light polarized along the long molecular axis. We have chosen to concentrate on the aromatic ring mode for studying the LC behaviour.

HiPco SWCNTs in E7 were investigated in standard cells for LCs for planar alignment, as in the dielectric spectroscopy experiment. A schematic of the cell and laser configuration is shown in figure 5. The laser beam was focused into the sandwiched LC film perpendicular to the substrates. The direction of the light polarization was set parallel to the director and since the LC molecules have positive dielectric anisotropy, this configuration gives the highest peak intensity owing to the largest induced polarization in this direction. The LC is switched by application of a square wave voltage of increasing amplitude with 1 kHz frequency. The polarization direction for the input beam is kept constant in all the experiments, parallel to the original, relaxed planar director, which gives the maximum intensity for the zero-field steady-state configuration. The reorientation of the process can be followed in the Raman spectrum by the decrease of the LC peak intensity occurring during the realignment of the molecules out of the substrate plane, corresponding to the highest polarizability configuration.

As reference, the reorientation of a pure E7 LC in a cell was also monitored as a function of applied electric field. In the image of figure 6, attention is drawn to the aromatic ring stretching mode positioned at about 1608.5 cm$^{-1}$. Voltage of increasing strength was applied in an analogous way to the dielectric spectroscopy experiment. Up to 1 V, the peak intensity remains basically constant, compatible with the molecules keeping their original alignment below the threshold. The peaks are analysed by fitting them with Lorenzian functions for estimating the peak position.
Figure 5. Schematic of the experimental configuration. The laser beam impinges perpendicular to the substrate plane of the cell filled with the LC and CNT mixture (the respective dimensions are not to scale). The laser polarization is set parallel to the orientation direction of the director in the steady state. (Online version in colour.)

Figure 6. The Raman peak associated with the stretching of the aromatic rings of LC molecules is plotted as a function of the applied field. The peak intensity is unchanged below the reorientation threshold, but dramatically decreases above it. (Online version in colour.)

and its area. At 1.5 V, the peak intensity starts to decrease, indicating that the molecules have started to change orientation. As the voltage is further increased, the peak intensity continues to decrease until a steady state, corresponding to homeotropic orientation, is reached. It is worth pointing out that the reorientational threshold appears strongly reduced compared with the dielectric permittivity measurements. The reason is that, for the case of switching probed by Raman spectroscopy, an AC field was used for driving the reorientation, while, for the other experiment, a DC field was applied. Although care was taken during the dielectric spectroscopy experiment in applying a field of opposite polarity for removing the charges built up on the electrodes, an accumulation of charge during the measurement is unavoidable. This reduces the effective applied field, thus requiring the application of a higher external field for achieving the LC reorientation.

The same approach was used to follow the Frederiks reorientation for the CNT-doped LC; we followed the reorientation of LC molecules by monitoring the magnitude of the LC peak. Also, in this case, the HiPco SWCNT-E7 LC mixture was filled by capillary action into standard cells for planar alignment and equipped with ITO electrodes, as in the previous experiments.
We show the analysis of the LC behaviour from regions where bundles were present with a noticeable difference in their size. Raman spectroscopy is widely used for investigating CNTs because of the characteristic peaks associated with structural and morphological characteristics such as defects, presence of amorphous carbon, nanotube diameter and much more [6]. In figure 7, the G bands of the HiPco SWCNTs are reported. These modes correspond to vibrations tangential to the tube walls. The most intense peak, located at 1595.7 cm$^{-1}$, has a position close to the aromatic stretching mode of E7 molecules, yet is clearly distinguishable as visible in figure 8.

**Figure 7.** An extract of the Raman spectrum of the HiPco SWCNTs showing the G band. The most intense peak is located at 1595.7 cm$^{-1}$, while the second main one is centred at 1556.5 cm$^{-1}$. These correspond to vibrations tangential to the CNT surface.

**Figure 8.** (a,b) In the images, we follow the reorientation of the LC by monitoring the selected Raman peak, the stretching mode of the phenyl rings of the LC molecules. The two time peaks are visible because of the presence of SWCNTs (left peak, G band), while the right peak is from the LC. The spectra have been recorded in the presence of CNT aggregates, small in (a) and very large in (b). Voltage of increasing strength has been applied to induce molecular reorientation, revealed by a decrease of the peak intensity. The threshold-like behaviour is distinguishable in (b), in which the LC peak area is plotted as a function of the applied voltage. The presence of the large CNT aggregate strongly affects the LC reorientational threshold. The value of the threshold is substantially increased, as visible in the figure by the unchanged peak area at a voltage much higher than the original Frederiks threshold of pure E7, indicating that the molecules remain at the original position. (Online version in colour.)
Figure 9. Plot of the fitted area of the Raman peaks shown in the previous images as a function of the applied voltage. The reorientational LC process can be easily followed in (a) for the pure E7 (filled black squares), E7 in the presence of small (filled circles) and large CNT aggregates (asterisks). In (b), we report the area of the G peak of SWCNTs for the case of small (filled circles) and large aggregates (asterisks), together with pure E7 (filled squares) as the reference. (Online version in colour.)

Although information strictly connected to CNTs is not crucial in our experiments, the presence of SWCNT peaks in our LC spectrum confirms the presence of SWCNTs exactly in the location of our investigations. In fact, in the sample doped with CNTs, as shown in figure 8, it is possible to recognize the signal from the G band of SWCNTs, the left peak, from the one of the LC, on the right. In the images, the reorientation of LC molecules is followed in the proximity of small (figure 8b) and very large (figure 8a) CNT aggregates. The reorientation of the LC appears strongly affected by the size of CNT bundles. We report the analyses from two different locations selected because the CNT bundles were optically visible and were clearly of different sizes, with one bundle being just barely visible, while the second appeared distinctively denser and darker than the first one.

The Raman spectrum of the area in which the smaller bundle was present was reported in figure 8b. By applying an electric field, we can follow the reorientation of the LC molecules in the location of the CNT bundle, the presence of which is revealed by the G band peak on the left. Plotting the peak area obtained by the fit, figure 9a, we note that the LC molecules reorient as in the pure sample, with no noticeable difference in the reorientation threshold.

On the other hand, when a bigger bundle is present, this can strongly affect the LC reorientation. As clearly visible in figure 8b, the LC peak at 5 V has the same intensity as the initial, steady-state value. This means that the molecules are unable to change their initial orientation, even when a voltage much higher than the threshold voltage of the pure E7 sample is applied. It is worth stressing that the pure LC has reached its fully switched position at voltages well below 5 V, while here no molecular reorientation apparently occurs. The molecules eventually reorient when increasing to a substantially higher value and appear fully switched at approximately 8 V. The key observation here is that the reorientational threshold increases significantly because of the presence of the bundle.

The behaviour described above is summarized in figure 9a, where the areas of the peaks for pure E7 and E7 doped with CNTs in the presence of small and large aggregates are plotted as a function of the applied electric field, for better comparison of the reorientational behaviour. For pure E7, the initial higher values correspond to planar orientation of the molecules followed by sharp decreases during the reorientation until homeotropic alignment is achieved, indicated by attainment of another plateau state with minimum peak intensity. The profile of the peak intensities follows the typical Frederiks threshold behaviour. Small bundles of CNTs do not have a remarkable effect on the reorientational behaviour of the LC, unlike larger aggregates, which visibly increase the threshold of the reorientation. In figure 9b, we report the behaviour of the
G band of the CNTs corresponding to the left peak in the eight images. In the case of small CNT aggregates, their Raman signal indicates that the nanotubes initially follow the LC reorientation. However, when the LC molecules are approaching a homeotropic orientation, the CNTs do not apparently follow any more, since the intensity of the G peak increases. For large aggregates, the behaviour of nanotubes is not clearly correlated to the LC behaviour, and the Raman CNT peak intensity slightly increases, while the corresponding LC peak decreases due to the reorientation. Since the aggregates are very large, it is probable that some looser tubes are in a frustrated state, which brings fluctuations in orientation.

We have shown that different LC molecules can interact differently with CNTs, which gives different results in dispersion quality. Moreover, the presence of surface interactions, and thus presumably of strong anchoring, can be visualized optically at the nematic–isotropic phase transition, as well as monitoring the Raman shift of radial breathing modes of SWCNTs in 5CB [35]. Since 5CB was shown to interact with HiPco SWCNTs, we can expect a similar behaviour for E7 also. The presence of such interactions implies that CNTs can also influence the order of LCs. Since CNTs have a large surface area, their aggregates provide a huge amount of available surface for LC molecules. We argue that large bundles, with their extremely large surface area, result in a great amount of LC molecules strongly anchored to the nanotube surfaces, hindering the reorientation of LCs and thus keeping the molecules in their original configuration until a substantially higher voltage is applied. This effect is definitely detrimental to the improvement of the display performance of the LC, and hence any such venture can only succeed if the dispersion is of very high quality.

Another important aspect of our experiments is that, following the behaviour of CNTs and LC at the same time under field applications, we can show that when CNTs are in aggregates, they cannot follow the reorientation of the LC because the orientation imposed by the aggregation cannot be easily overtaken. This demonstrates that either when doping LCs with CNTs or manipulating CNTs with LCs, the dispersion quality is of key relevance, and bundles have to be strongly avoided.

5. Conclusions

In conclusion, our systematic investigation of CNT doping of nematic LCs shows neither a change in dielectric anisotropy nor a reduction in the switching threshold. A type of MWCNT sample produced essentially no change to these parameters, but all other CNTs had more or less adverse effects. We were unable to reproduce the reported positive effect from the doping of CNTs, indicating that these were not an intrinsic feature of the composite. Since previous work reporting positive effects of doping has often involved rather tough mechanical treatment of the CNTs, the dopants in these cases may then have been composed of short fragments of defect-rich nanotubes. Studies of LCs doped with CNTs that have been damaged or shortened in a controlled way are required to verify whether such particles could be the origin of the reported positive effects.

Our experiments prove the adverse effect of the presence of CNT bundles. In fact, if these are present, they can strongly increase locally the LC reorientation threshold and contribute to altering the average, overall properties in an undesirable way. The preparation process should thus be aimed at avoiding the presence of CNT bundles.

It is clear that LCs can interact well with the CNT surface, and this property can be extremely useful for new functional systems combining the high response and unique organizing skills of the LC with the undoubtedly exceptional properties of CNTs. A better control on the CNT type and purity would provide an added value, which would then allow a fine tuning of the composite properties organized by the anisotropic fluids. In this way, not only are composites useful for display applications, but also new multi-functional and organized structures can be created that possess controlled properties in direction, position and magnitude.
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