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INVITED ARTICLE

Dispersion and orientation of single-walled carbon nanotubes in a chromonic liquid crystal

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A post-synthesis alignment of individual single-walled carbon nanotubes (SWCNTs) is desirable for translating their unique anisotropic properties to a macroscopic scale. Here, we demonstrate excellent dispersion, orientation and concomitant-polarised photoluminescence of SWCNTs in a nematic chromonic liquid crystal. The methods to obtain stable suspension are described, and order parameters of the liquid crystal matrix and of the nanotubes are measured independently.

Keywords: single-walled carbon nanotubes; nematic liquid crystal; alignment

1. Introduction

Carbon nanotubes (CNTs) are high aspect ratio tubular objects comprising single-walled carbon nanotubes (SWCNTs) or multiple concentric walls (MWCNTs). The CNTs, and especially SWCNTs, display remarkable mechanical, optical, thermal and electrical properties.[1] Exploiting them offers new opportunities for materials and related devices including multifunctional polymer composites,[2,3] aligning layers,[4] protective textiles,[5] optoelectronics,[6,7] and field emission transistors.[8] Applications of CNTs at the macroscopic scale, however, require the translation of the anisotropic properties of the tubes to the ensemble level.[9–11] To this end, a variety of approaches have been explored.

Perhaps the most straightforward approach is synthesis of aligned nanotubes on substrates.[12] Despite progress, however, time-consuming procedures, limited control of the type of tubes produced, and the presence of catalyst impurities render this technique still unsuitable for most industrial applications. A qualitatively different approach, which we will employ herein, relies on post-growth [13] processing, whereby CNTs are first individually exfoliated in suspension and subsequently

aligned.[14,15] To date several schemes have been demonstrated to overcome the strong, intrinsic van der Waals attraction between CNTs (especially between SWCNTs). In water, one set of techniques wraps the tubes with surfactants [16] or macromolecules [17,18]; another set of techniques employs acid-oxidation [19] or acid-protonation [20] of tubes. A third set reduces nanotubes with alkali metals to form polyelectrolytes, which are soluble in polar organic solvents.[21] After the tubes are suspended, macroscopic alignment of the ensemble is required. In semisoft solids, permanent alignment can be obtained by mechanical deformations (e.g., shrinking of gels [22] and stretching of polymers [6,23]). In isotropic liquids, it is possible to align CNTs using mechanical shear, but resultant orientational order is transient. Magnetic fields have also been used to orient tubes, but alignment was not substantial.[24,25]

In a different vein, structured solvents such as liquid crystals have frequently been considered as matrices to achieve a stable and easily switchable macroscopic orientation of CNTs (see [26–33] and references therein). Nematic thermotropic liquid crystals are attractive for this purpose, due to their

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fluidity and their susceptibility to external fields. Unfortunately, dispersion of individual nanotubes is not straightforward in thermotropic liquid crystals; bundling and re-aggregation are usually observed [30–33] even for mild concentrations of SWCNTs. Water-based lyotropic liquid crystals, on the other hand, offer a novel structured fluid system that is compatible with water-dispersed CNTs. Indeed, small bundles of nanotubes have been dispersed and aligned in surfactant- and discotic-based lyotropic liquid crystals at CNT concentrations of up to 0.2 wt.%. [30–33] While significant progress was made in this work, the degree of nanotube alignment was limited, either due to the low-order parameter of the lyotropic systems or the probable presence of small and disordered bundles. The highest order parameter reported for SWCNTs in bulk nematics, $S \sim 0.6$, was obtained in a lyotropic liquid crystal. [31] Such measured order parameter is insufficient to fully exploit the very strongly anisotropic properties of SWCNTs. It is also well below the maximum value predicted by taking into account the nematic elastic and anchoring torques acting on individual tubes. [34] Another drawback of the systems explored thus far is the difficulty to orient large domains. Finally, the persistence of individual SWCNT's properties, especially optical ones, in these systems has not been quantitatively demonstrated.

In the present contribution, we overcome three of these drawbacks by dispersing SWCNTs in nematic chromonic liquid crystals (NCLCs). This new class of water-based lyotropic liquid crystals [35–37] provides an excellent host for individual SWCNTs with surface-aligning potential. Using ultra-centrifugation, we were able to obtain a dispersion of individual SWCNTs in nematic CLCs as demonstrated by a strong photoluminescence specific to individual tubes. Polarised Raman spectroscopy and optical birefringence were then employed to independently measure the nanotube and the NCLC order parameters. [38,39] The value of the SWCNT order parameter was found to be very high, $S^{\text{CNT}} \sim 0.9$, i.e., in the same range as the values of the host NCLC. We further show, for the first time, that a spontaneous and almost perfect alignment of individual SWCNTs can be achieved using NCLCs.

2. Materials and methods

2.1 Preparation of materials

2.1.1 SWCNTs solutions

The CNTs were first exfoliated under strong tip-sonication in an aqueous DNA solution, where DNA wrapping takes place with π – π stacking interactions followed by a helical stranding. [40]

The tubes were synthesised by the HipCo process and purchased from UNYDIM (California, USA).

They have a diameter distribution from 0.7 to 1.3 nm and are assembled in bundles. Salmon DNA was supplied by Nippon Chemical Feed Co. Ltd (Japan). SWCNTs (0.4 wt.%) were first mixed in the aqueous solution of denatured DNA (0.2 wt.%). The mixture was subsequently tip-sonicated in an ice-water bath for 2 h using a Branson homogeniser, Sonifier model S-250A associated to a 13-mm step disruptor horn and a 3-mm tapered microtip, operating at a 20-kHz frequency. The sonicator power was set at 20 W and delivered by pulses of 0.5 s separated by 0.2-s intervals at rest. The resulting solution was centrifuged at 3000g for 30 min to remove amorphous carbon aggregates and other residual impurities. Some samples were ultra-centrifuged twice for 2 h each time at room temperature in a Beckman Optima LE-80K ultracentrifuge (Beckman Coulter Inc., CA, USA). The first centrifugation was carried out at 16,556g then the resulting supernatant was kept and subsequently centrifuged at 66,225 g, finally the supernatant was collected and used in experiments. In both cases, the final concentration in SWCNTs was obtained by absorbance measurements in the 500–900-nm range with a Varian Cary 50 spectrophotometer.

2.1.2 Preparation of the chromonic suspensions

Di-sodium cromoglycate (DSCG) of chemical name 5,5'-[(2-hydroxy-1,3-propanediyl) bis(oxy)] bis [4-oxy-4H-1-benzopyran-2-carboxylate] and chemical formula $\text{C}_{23}\text{H}_{14}\text{O}_{11}\text{Na}_2$ was purchased from Sigma-Aldrich and was first purified by dissolving it in Milli-Q water at 60°C, filtering the suspension through a 0.45- μm cellulose acetate membrane and then drying the filtered solution. The purified DSCG powder was then mixed either with water or with the SWCNT-DNA suspension and magnetically stirred at room temperature for 12 h.

2.2 Measurements

Conventional sandwich-type cells commercially available from EHC Company (KSRP-06-B111P6NSS), Ltd, Japan, were used to align the chromonic liquid crystals (either doped or not). The cells were sealed after filling with araldite glue to avoid water evaporation. The cells were observed with a polarising microscope (Leitz 12 POL S) equipped with a 1024×768 pixels Sony CCD camera and an Instec hot stage regulated at 0.1°C. Local birefringence measurements were performed with a Leitz Berek Compensator B under monochromatic irradiation at 584 nm.

The samples were also examined with Raman and photoluminescence spectroscopies using a Bruker

RFS100 FT-Raman spectrometer equipped with a nitrogen-cooled germanium detector. The excitation source is a continuous Nd-YAG laser emitting at 1.16 eV (1064 nm). Excitation at 1.16 eV permits simultaneous observation of photoluminescence and the Stokes Raman signals (Raman shift in the range $100\text{--}3500\text{ cm}^{-1}$, i.e., energy of scattered photons in the range 1.15–0.75 eV).

3. Results and discussion

3.1 Phase diagram

DSCG molecules are formed by two rigid heterocycles connected by a flexible bridge (Figure 1a). These molecules spontaneously form linear aggregates in water (Figure 1b). Note that the detailed microstructure of these aggregates has been a subject of some controversy, e.g., regarding the number of DSCG molecules [35–37] in the cross-section of a single aggregate and whether these molecules are strongly tilted on average [41] or are perpendicular to the aggregate axis. According to X-ray scattering data,[42,43] the ratio of the area of the aggregate cross-section to the molecular area of DSCG is close to two. Scanning transmission X-ray microscopy [44] and sample behaviour in the magnetic field [45] further demonstrate that the

aromatic planes of DSCG molecules are, on average, perpendicular to the director and the aggregate axes.

When mixed in water, DSCG self assembles into a nematic phase at room temperature for concentrations between 12 and 18 wt.% (Figure 1c). When prepared with the SWCNT suspensions, the same phase diagram for the modified DSCG solutions was obtained, indicating that doping with a low SWCNT concentration (typically smaller than 0.1%) does not significantly disturb the DSCG interactions. The quality of the nematic liquid crystal, however, strongly depends on the nature of the SWCNT dispersion. In a first set of experiments, the SWCNT solution appeared homogeneous under an optical microscope but was not ultra-centrifuged. After addition of DSCG and stirring at room temperature for a period of 12 h, only in samples with a low final SWCNT concentration ($<0.001\text{ wt.}\%$) did the final DSCG-SWCNT solutions remain homogeneous at optical resolution,. In samples more concentrated in SWCNTs, increasing numbers of aggregates were visible in the microscope within a few days. Such aggregates were absent when the SWCNT dispersion is ultra-centrifuged before adding DSCG. We were thus able to prepare stable and homogeneous SWCNT-doped liquid crystals up to 0.027 wt.% SWCNT. In the following, the DSCG concentration

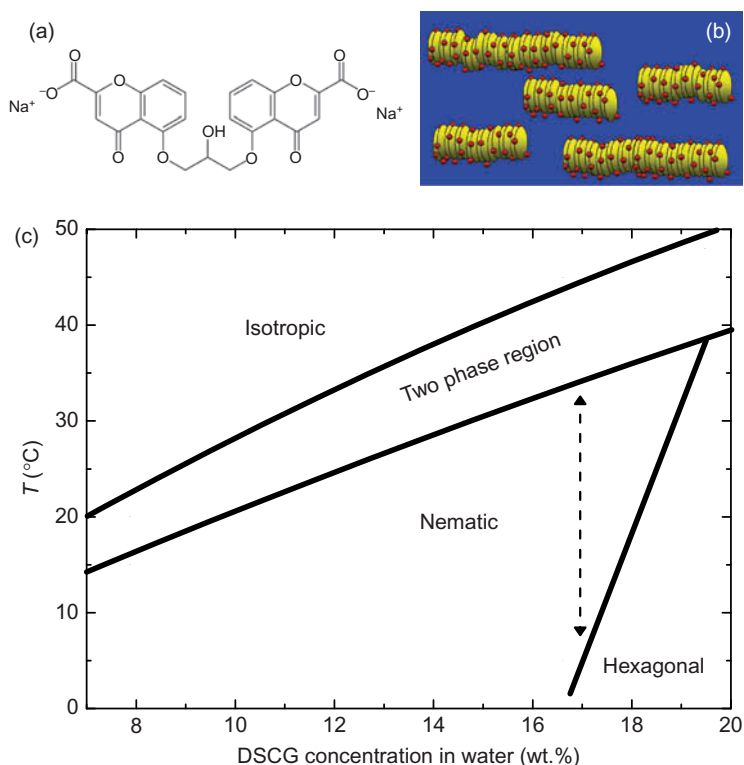


Figure 1. (colour online) (a) Chemical structure of DSCG molecule. (b) The flat molecules stack into columnar aggregates forming a nematic phase. (c) Phase diagram of DSCG aqueous solutions, redrawn from Ref. [50].

was fixed at 17 wt.%, a concentration for which the nematic phase (arrow in Figure 1) is stable between 5°C (nematic-columnar phase transition) and 32°C (nematic-isotropic phase transition).

3.2 Individual nanotubes

We confirmed that the tubes were individually dispersed with near-infrared photoluminescence excitation (PLE) spectroscopy.[38,39,46] The latter method is a nondestructive and powerful technique by which to probe the aggregation state of CNTs in solution: in bundles, the semiconducting tube photoluminescence is quenched because of energy transfer to neighbouring metallic nanotubes. We derive PLE maps by exciting the samples in the visible range 550–850 nm and by collecting its emission in the near-infrared range 950–1350 nm. On the PLE maps (Figures 2a and 2b), different CNTs species are identified and labelled with their chiral indexes (n,m).[47] No significant peak shifts were observed when comparing the PLE maps of SWCNTs in water and in the NCLC suspensions; this observation is indicative

of a comparable local dielectric environment. The NCLC-doped solution also exhibited an increase of the PLE intensities for the largest wavelengths (i.e., for the largest nanotube diameters) compared to the smaller wavelengths (i.e., for smaller nanotubes). This feature may be assigned to some contacting between semiconducting nanotubes in tiny bundles, resulting in energy transfer from large bandgap to small bandgap nanotubes.[46] Nevertheless, as the general PLE signal remains strong when nanotubes are dispersed in the NCLC, we can conclude that re-aggregation in the samples is not substantial.

More quantitatively, coupled Raman and photoluminescence measurements were also carried out using the FT-Raman spectrometer with an excitation line at 1064 nm. This scheme enables us to superimpose the photoluminescence signatures between 1100 and 1700 nm and the Stokes part of the Raman spectra. For all of the suspensions of CNTs, the Raman features are characteristic of SWCNTs. They exhibit radial breathing modes (RBMs) at $\sim 270\text{ cm}^{-1}$, a D-band at $\sim 1250\text{ cm}^{-1}$, and a G-band at $\sim 1590\text{ cm}^{-1}$ (Figure 2c). These findings further suggest that the

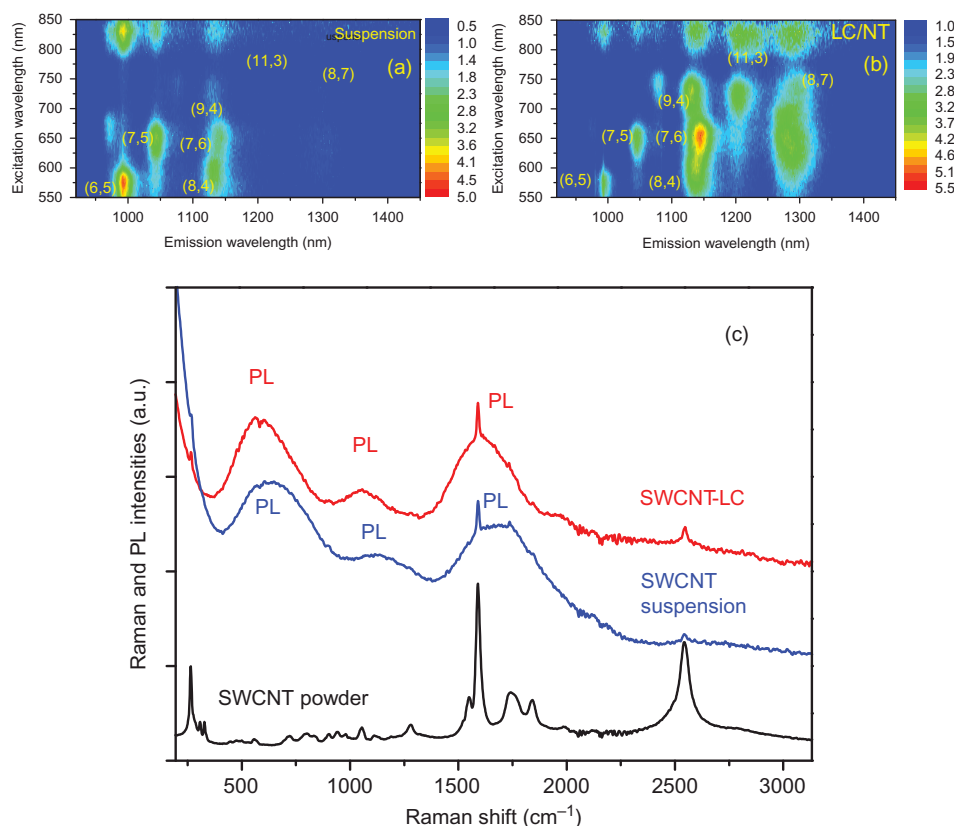


Figure 2. (colour online) PLE maps for (a) DNA/SWCNT suspension in water and (b) DNA/SWCNT in DSCG; (c) Typical superimposed Raman and photoluminescence spectra excited at 1.16 eV. The broadest lines are assigned to photoluminescence, as indexed on the figure. From bottom to top: powders, aqueous suspension and DNA/SWCNT-DSCG suspension. All spectra were normalised with respect to the intensity of the G-band and shifted along the vertical axis for clarity.

nanotube properties are not altered during preparation of the suspensions. In addition, Raman and photoluminescence profiles are very similar for SWCNTs in aqueous suspensions and in the NCLC, with no significant Raman or photoluminescence peak shifts and similar intensity ratios between Raman peaks and photoluminescence signal (see Figure 2c). These results indicate that both suspensions contain primarily individual CNTs and, as expected, that their local dielectric environment is essentially the same. Taken together all of the spectroscopic measurements indicate a good dispersion of individual SWCNTs in the NCLC host suspension.

3.3 Alignment of SWCNTs and order parameters

We used the orientational field of the NCLC to align SWCNTs. A uniform alignment of the NCLC is obtained in standard polyimide cells.[48,49] In 6 μm thick cells, the director of the SWNT-doped NCLC is also uniformly oriented along the rubbing direction as shown by polarising microscopy (planar alignment shown in Figure 3a). The orientation of the nanotubes in the DSCG matrix is then studied using polarised Raman and photoluminescence measurements. The nematic order parameter S of rods is defined by the statistical average $\langle 3 \cos^2 \theta - 1 \rangle / 2$, where θ is the angle of a rod with respect to the average orientation. For individual tubes, the SWNT order parameter S^{CNT} can be simply obtained [38,39] from the Raman and photoluminescence-polarised intensities of three different configurations VV, VH and HH, where the first and second symbols in this notation correspond, respectively, to the incident and scattering polarisation. The V and H notations indicate orientations of the polarisation, respectively, parallel and perpendicular to the liquid crystal director.

The polarised coupled Raman and photoluminescence spectra of the SWCNTs in the uniaxial environment of the oriented liquid crystal cell are reported in Figure 3b. The spectroscopic signals are strongly polarised, with a maximum intensity for the VV configuration when the polarisations of the incident and scattered light are both parallel to the NCLC director. By contrast, HH and VH configurations give very weak signals. These results show that the average orientation of the SWCNTs is parallel to the NCLC director. The order parameter S^{CNT} was calculated from Ref. [38,39]:

$$S^{\text{CNT}} = \frac{3I_{VV} + 3I_{VH} - 4I_{HH}}{3I_{VV} + 12I_{VH} + 8I_{HH}} \quad (1)$$

(Note: We checked that the absorbance and birefringence of the liquid crystal cells were small enough to

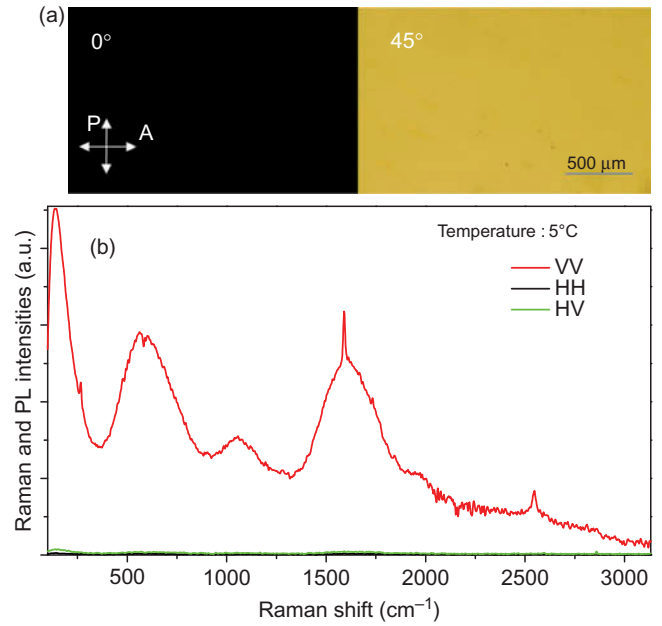


Figure 3. (colour online) DNA/SWCNT suspensions in DSCG studied in a cell (6 μm) made by two parallel rubbed polyimide substrates. (a) Snapshots of cells observed by polarised optical microscopy at two different angles (0° left, 45° right) of the rubbing direction with respect to the polariser orientation. Also indicated are the angles (0° in the left picture and 45° in the right one) between the polyimide rubbing direction and the polariser, respectively; (b) polarised Raman and photoluminescence spectra of the same sample, excited with a laser line at 1064 nm. In red the VV component consisting of both incident and scattered polarisations parallel to the rubbing direction. In green and blue the components HV and HH having, respectively, one or two polarisation vectors perpendicular to the rubbing direction.

apply Equation (1)). The three spectra (VV, HH and VH) display similar profiles and can be superimposed by a simple normalisation; we thus measured the two ratios I_{VH}/I_{VV} and I_{HH}/I_{VV} in the total spectra range and obtained the value of S^{CNT} reported in Figure 4 with a small relative error (<4%). The typical order parameter is $S^{\text{CNT}} = 0.9$, an unusually large number. To our knowledge this value for the order parameter is the highest ever obtained for SWCNTs in a lyotropic liquid crystal.[26–33] Additionally, nanotube orientation is completely lost for temperatures above 32°C when the DSCG enters into its isotropic phase.

We next compared the order parameter of the nanotubes with that of the host DSCG obtained from optical retardation measurements. The optical path difference δ between ordinary and extraordinary components of transmitted light is related to the liquid crystal order parameter S^{LC} and to the cell thickness d via the expression $\delta = \alpha d S^{\text{LC}}$, where α is a numerical coefficient related to the optical polarisability of the medium. We checked that δ for pure DSCG and for

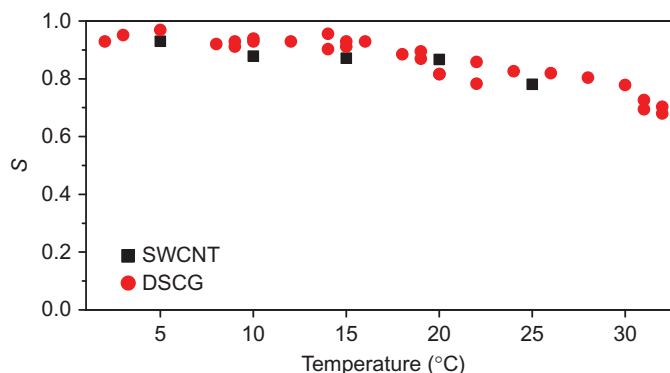


Figure 4. (colour online) Order parameters of the DSCG (S^{LC}) and of the SWCNT (S^{CNT}) for the DNA/SWCNT suspension in DSCG obtained in a 6- μm thick cell with rubbed-polyimide alignment layers.

DNA/SWCNT-DSCG is the same in identical cells; no change due to the presence of the nanotubes' guest particles was observed. The coefficient α was obtained by measuring δ at the temperature $T = 5^\circ\text{C}$ in the nematic phase, close to the nematic/hexagonal phase transition for which $S^{LC} = 0.97$ has been found by NMR experiments [50]. In Figure 4 we show the temperature dependence S^{LC} of the DSCG. The slight decrease observed in the order parameter by increasing the temperature from 2°C to 32°C is probably due to the shortening of DSCG aggregates and change in their length distribution.[48–51]

The order parameter of nanotubes is thus found to be substantially similar to that of the DSCG liquid crystal solvent. The SWCNTs length, L , after sonication and ultra-centrifugation treatments, is typically a few hundreds of nanometres,[52,53] slightly larger than the typical length of DSCG columns (a lower bound value of 20 nm was found at the isotropic-nematic phase transition [48,49]). All the SWCNTs interact with DSCG columns. The orientational order of the shortest tubes with length in the same range as the DSCG columns simply reflects the statistical orientational disorder of the neighbouring DSCG columns. Longer liquid crystals nematogens would have yielded a smaller SWCNTs order parameter, as it has been observed for tubes dispersed in the nematic phase of colloidal suspensions of micrometer-sized rod-shaped viruses.[54]

Interestingly, had we considered the opposite limit of long ($L \approx 1 \mu\text{m}$) and rigid SWCNTs in a continuous DSCG director field, the tubes would still not have been perfectly aligned due to the finite nematic elasticity and/or anchoring energy.[34] For example, in the case of finite anchoring, a tube of radius a rotating of a small angle θ in the uniform DSCG director field yields a typical anchoring cost of $2\pi aW \theta^2$ per unit length, where W is the anchoring energy coefficient of DSCG at the surface of the tube.

The probability distribution function $f(\theta)$ then follows the distribution: $f(\theta) \propto \theta \exp(-2\pi aWL\theta^2/k_B T)$, where k_B is the Boltzmann constant. This yields an order parameter $S \approx 1 - 3 k_B T / 4W\pi aL$. For typical values, $a \sim 1 \text{ nm}$, $T \sim 300 \text{ K}$, $S \sim 0.9$, $L \sim 0.1 - 1 \mu\text{m}$ this expression gives a value for the anchoring coefficient $W \sim 10^{-6}$ to 10^{-5} J.m^{-2} , comparable to the weak anchoring coefficient of DSCG on silane-treated glass.[45]

3. Conclusion

In conclusion, we have shown that a lyotropic chromonic liquid crystal can be used to align individual SWCNTs over stable macroscopically large domains. The CNTs remain individual in a DSCG nematic phase, when the liquid crystal is prepared from an ultra-centrifugated SWNT dispersion. The individual CNTs align parallel to the liquid crystal director with an order parameter of approximately 0.9, the largest ever measured in SWNT suspensions. These findings suggest a new paradigm for efficient translation of the anisotropic properties of individual nanotubes to macroscopic materials. In addition, the relative large susceptibility to the electric field of the chromonic liquid crystal opens up to the possibility of orientational switching of these nanotubes' suspensions and to their use as constituents in smart materials.

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