Spontaneous macroscopic carbon nanotube alignment via colloidal suspension in hexagonal columnar lyotropic liquid crystals

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Abstract

The self-assembly of amphiphilic molecules in aqueous solution into lyotropic liquid crystals (LCs), characterised by soft yet long-range ordered nanoscale structures, constitutes a fascinating phenomenon at the heart of soft matter science which can be employed in a manifold creative ways. Particularly interesting structures may arise as a result of functionalization of the LC with appropriate guest molecules, adopting the order of their host. Here we combine cat- and anionic surfactants to form a liquid crystalline colloidal suspension of carbon nanotubes (CNTs), which by virtue of the spontaneously formed hexagonal columnar LC structure are uniaxially aligned over macroscopic areas. The nanotube concentration can be so high, with sufficiently uniform alignment, that the mixture becomes a fluid linear polariser, the anisotropic optical properties of CNTs having been transferred to macroscopic scale by the LC. Moreover, thin and highly aligned filaments can be drawn and deposited in selected directions on arbitrary surfaces, after which the LC template can be rinsed away. Combined with recently developed methods for CNT fractionation according to chirality, the technique would yield an unprecedented degree of control in the practical realization of carbon nanotube-based devices and materials.

Introduction

When dissolved at sufficient concentration in water, amphiphilic molecules such as surfactants self-assemble into lyotropic liquid crystals (LCs), anisotropic fluid phases characterised by the counterintuitive combination of high molecular mobility and long-range order, orientational and often also translational. Various types of LC are currently attracting much interest in diverse fields of research and technology, their presence in modern materials science being particularly strong. The soft but ordered LC structures offer unique opportunities for designing new functional nano- or microstructured inorganic[1], organic[2] or composite[3-5] materials. Here we focus on the latter category, employing a lyotropic LC phase as a self-organized fluid nanotemplate, providing a straightforward and non-discriminative means of aligning unsupported carbon nanotubes (CNTs) over macroscopic areas.

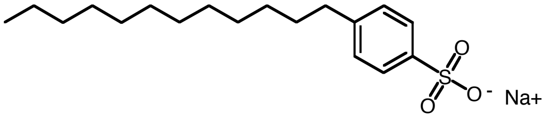
The outstanding chemical and physical properties of CNTs are today well established[6], with numerous innovative applications proposed in fields ranging from nanoelectronics to functional composites to pharmacology, but large-scale production of CNT-based technology is in most cases hampered by a few practical issues. One of these is the difficulty in controlling the nanotube orientation, a crucial requirement for many materials and devices. Important achievements in terms of growing CNTs on a substrate with control of orientation have been reported, perpendicular to the substrate in so-called forest growth[7] as well as parallel to the substrate[8]. While truly impressive, these approaches are not applicable to substrate-free synthesis methods such as the HiPco process[9] for growing single-wall tubes (SWCNTs) or any of the methods used for growing multi-wall tubes (MWCNTs) on commercial scale. Moreover, single-wall CNT forest growth is a highly non-trivial venture. Finally, since no growth method to date allows control of CNT chirality (the roll-up direction of the graphene sheet in the nanotube), these alignment methods are of little use when nanotubes with specific electronic properties—determined by the chirality—are required. Thus, an efficient method for aligning unsupported CNTs, versatile enough to work with any nanotube type and to allow orientation in any desired direction, is of great interest in the practical processing of carbon nanotubes.

A most promising approach to achieve this goal is to prepare a colloidal suspension of the nanotubes in a liquid crystalline host, relying on its spontaneous long-range orientational order to align the CNTs[4, 5, 10-14]. While initial attempts using thermotropic nematic (display-type) LCs were limited to low CNT concentration and offered no simple means of removing the LC once it has played its aligning role[5, 10-12], we recently demonstrated that a surfactant-based lyotropic nematic LC phase aligns the CNTs equally well while generally providing better dispersion, thus allowing for higher nanotube loading, and we pointed out that lyotropic LCs can easily be rinsed away once they are no longer desired[4, 13]. In the present work we use a different, more complex lyotropic host, combining cat- and anionic surfactants in a hexagonal columnar LC phase, thereby changing the properties of the colloidal CNT suspension in a most favourable way. We achieve a 20-fold increase in nanotube concentration while maintaining good dispersion and macroscopic-scale control of the tube orientation, resulting in striking new optical properties. Moreover, while our previous study was limited to samples confined in glass capillaries, the new mixture allows easy drawing of highly aligned thin filaments, giving this system excellent possibilities for handling and processing. This opens a new way towards easy and cheap fabrication of devices requiring carbon nanotubes deposited on substrates, aligned along selected directions.

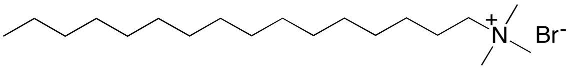
Results and discussion

The standard method of dispersing CNTs is to add them to an aqueous surfactant solution which is then subjected to ultrasonication. The best results are generally achieved using ionic surfactants with aromatic components, such as the anionic sodium dodecyl benzene sulphonate (SDBS, *cf.* Table 1), with which as much as 20 mg/mL carbon nanotubes have been reported to be individually dispersed[15]. We therefore chose to work with SDBS when dispersing our CNTs, which were of HiPco single-wall type. For our purposes, a drawback with SDBS is that little is known about its ability to form LC phases, the few reports where this has been described dealing with mixtures of SDBS and other surfactants and generally with focus on vesicle formation in the dilute limit[16]. We therefore chose to use a different surfactant for building up the LC phase.

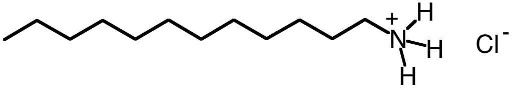
Table 1. Surfactants discussed in the work.



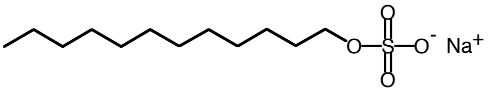
Sodium Dodecyl Benzene Sulfonate (SDBS)



Hexadecyl (Cetyl) Trimethyl Ammonium Bromide (CTAB)



Dodecyl Ammonium Chloride (DdACl)



Sodium Dodecyl Sulfate (SDS)

Initial tests with the SDBS-similar surfactant sodium dodecyl sulphate (SDS) were unsuccessful as the addition of SDS induced strong aggregation of the CNTs (Fig. 1a). This can be understood as a result of depletion attraction; since the added SDS micelles have the same effective surface charge as the SDBS-coated CNTs they are electrostatically repelled from the nanotubes, hence they act as a depletion agent[17]. We thus switched to an LC host formed by cationic surfactants, the micelles of which will be electrostatically attracted to the CNTs, thereby not enhancing the depletion attraction between nanotubes. Indeed, we obtained much better results with both dodecyl ammonium chloride (DdACl) and cetyl trimethyl ammonium bromide (CTAB), *cf*. the example in Fig. 1b. In the following, only the results with CTAB as LC-forming surfactant are described.

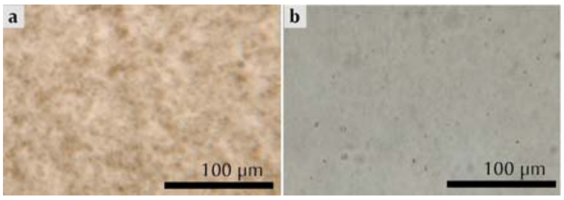


Fig. 1. a: Aggregating SDBS-coated CNTs at a concentration of 0.05 wt.-% in an SDS-based nematic LC phase, observed in unpolarised light. b: The texture of the hexagonal columnar CTAB+CNT+SDBS+ water mixture **1** (0.2 wt.-% CNTs, i.e. 4 times the concentration in the left photo) used in the present work.

Although SDBS is a monovalent salt, its strong adsorption onto the nanotube surface[15] makes the SDBS+CNT system in some respects comparable to a polyelectrolyte, giving our cat-anionic CNT suspension certain similarities with that of DNA (an anionic polyelectrolyte) complexated by cationic lipids, a combination studied by Rädler et al.[18]. The driving force for complexation was in their case the entropic gain from the release of counterions into solution, made possible by the condensation of cationic lipid and DNA. We believe a similar situation prevails in our system. A negatively charged dodecyl benzene sulphonate-ensheathed nanotube can be closely surrounded by positively charged rod-shaped micelles of cetyl trimethyl ammonium, the counter ions of the surfactant molecules involved in the condensate being released in solution. A detailed discussion of these issues will be published separately

Most studies were carried out on an aqueous mixture (in the following referred to as Mixture **1**) composed of 28 wt.-% CTAB, 0.2 wt.-% single-wall carbon nanotubes (SWCNTs), and 1 wt.-% SDBS. Fig. 1b shows the microscopy texture of this mixture, from which it is clear that the CNT bundle size was small (the features seen in the texture are of a type and size that is typical of defects in a lyotropic LC texture, hence they may or may not be CNT aggregates). While a small degree of CNT aggregation probably was induced when adding the dry CTAB to the isotropic CNT suspension to produce mixture **1** (see Experimental), no large-scale aggregates or CNT network formation could be identified. Optimization of composition and sample preparation procedure should further diminish aggregation. Nevertheless, already at this stage the result must be considered as highly satisfactory, keeping in mind that we have increased the CNT concentration by 20 times with respect to our previous study[4, 13]. This success can most likely be attributed mainly to the reduced importance of depletion attraction and the benefits from cat-anionic complexation resulting from the use of oppositely charged surfactants for CNT dispersion and LC formation, respectively.

By means of small-angle x-ray scattering experiments we could conclude that mixture **1** forms a liquid crystal phase of hexagonal columnar nature, *cf*. Fig. 2. Two peaks are clearly visible, their scattering angles corresponding to lattice spacings d_{10} = 62.0 Å and d_{11} = 35.9 Å. The lattice spacings are related by a factor $1/\sqrt{3}$ as expected for the (10) and (11) reflections of a hexagonal columnar phase[19]. These data yield a lattice constant of the columnar structure of $a \approx 72$ Å (see inset of Fig. 2 for a graphical representation of lattice spacings and lattice constant), a value which compares well with data for binary CTAB + water hexagonal phases at similar surfactant concentration[20]. A columnar structure with such large lattice constant should be able to accommodate the HiPco single-wall CNTs, having a typical diameter of about 1 nm, without much problem. The exact morphology of the surfactant sheath surrounding the CNTs is still an open issue, and it seems to depend on the details of sample preparation, but we can assume that the maximum diameter of a CNT-containing micelle will be twice the length of the surfactant molecule plus the nanotube diameter (we do not consider any diffuse shells of counterions since they, as motivated above, are expected to be absent in the case of cat-anionic complexation). Considering an SDBS molecule length of about 2.5 nm and individually dispersed SWCNTs this would yield a micelle diameter of about 6 nm, still well below the lattice constant.

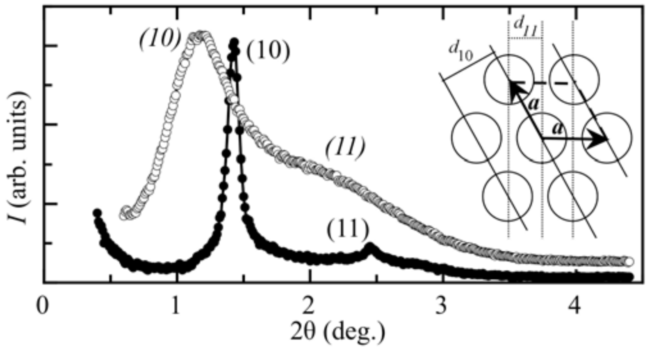


Fig. 2. Small-angle x-ray scattering intensity I as a function of scattering angle 2θ for the hexagonal LC phases formed by the CNT-containing mixture **1** (filled symbols) and the corresponding CNT-free mixture **2** after equilibration (empty symbols). Inset drawing defines the layer spacings d_{10} and d_{11} and the lattice constant a.

Multiwall carbon nanotubes (MWCNTs), containing a large number of graphene layers in each tube and therefore having a diameter of tens of nanometers, would apparently be too thick to easily fit in the lattice of this particular hexagonal lyotropic LC host phase. The same holds for bundles of SWCNTs. One cannot rule out that the nanotubes in these cases would constitute an important disturbance to the LC, but this could be resolved by choosing a different LC-forming molecule (e.g. a block co-polymer) that produces a hexagonal columnar phase with adequate lattice parameter. On the other hand, provided that the number of CNT-containing micelles is much less than that of the CNT-free micelles forming the LC phase, even the CTAB host phase can probably accommodate also these bulkier guests, their presence creating only local distortions of the hexagonal structure. The likely presence of small SWCNT bundles in the present study supports this view. Experiments with MWCNTs will be carried out in our labs in the near future.

We also prepared a CNT-free reference mixture (mixture **2**) with the same composition of SDBS, CTAB and water as mixture **1**. This initially developed an isotropic liquid phase, slightly viscous but with no signs of optical birefringence, even under moderate shear. After some days of equilibration at 40°C, however, a birefringent LC phase developed, also this of hexagonal columnar type albeit with a very small correlation length, as evidenced by extremely broad x-ray diffraction peaks, *cf.* Fig. 2. The system should probably be regarded as clusters with hexagonal columnar order rather than as a regular bulk LC phase. Despite the diffuseness of the peaks, a lattice constant of $a \approx 88$ Å could be estimated, considerably larger than for the system with nanotubes. Obviously, the presence of CNTs in mixture **1** has an important impact on the LC phase formation. Within our model that a CNT-containing SDBS micelle in effect acts as a polyelectrolyte, the SDBS and CTAB molecules do not mix easily, leading to the immediate formation of a CTAB-based LC phase in mixture **1** which basically maintains the structure of a similar mixture without SDBS and CNTs. In the nanotube-free mixture **2**, on the other hand, SDBS mixes with CTAB on a molecular scale, thereby severely obstructing the LC formation.

Fig. 3a-e shows optical microscopy textures of mixture **1**, taken shortly after preparation and gentle vacuum filling into an optically flat glass capillary. As is obvious from the photos taken with the sample between crossed polarisers (Fig. 3a-c) the fluid was optically birefringent, confirming its liquid crystalline state. Moreover, the filling procedure had ensured a quite uniform alignment with the director (the average direction of the principal symmetry axis of the rod-like surfactant micelles, defining the optic axis of the anisotropic LC medium) mainly along the capillary axis.

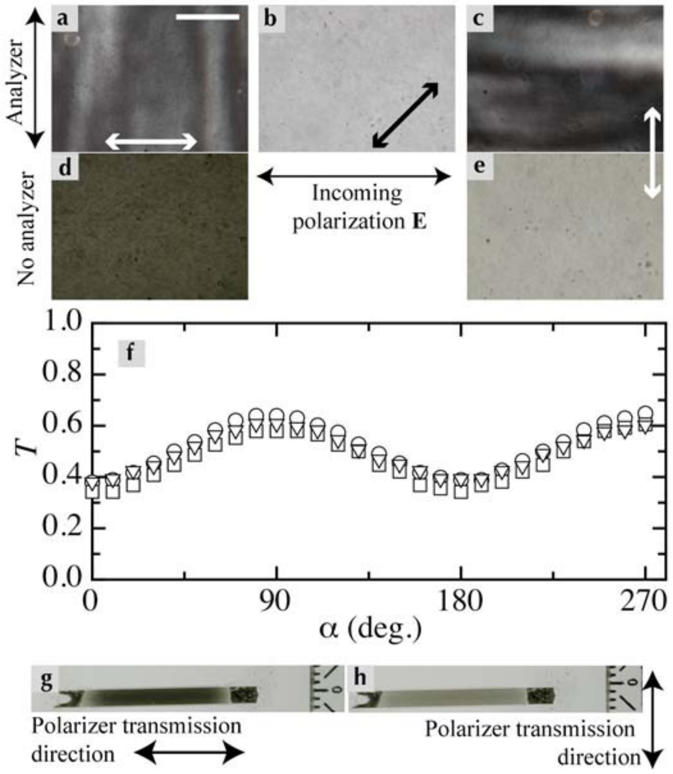


Fig. 3. a-e: Optical microscopy textures of a 200 μm thick capillary filled with the LC-aligned SWCNTs (mixture **1**), illuminated with light polarised horizontally; a-c: between crossed polarisers, the director (double-headed arrow) parallel (a), at 45° (b) and perpendicular (c) to the incoming light polarisation; d-e: textures without analyser corresponding to (a) and (c). Scale bar: 100 μm. f: Light transmittance *T* through the capillary as a function of angle α between the capillary axis and the polarisation direction of the incoming light, as measured with 633 nm (rings), 546 nm (squares) and 450 nm (triangles) wavelength. g-h: Macroscopic appearance of the capillary observed through a linear polariser held with its transmission direction parallel (left) and perpendicular (right) to the capillary axis, and thus to the LC director. The scaling to the right of the photos is in millimetres.

When studying the optical textures without any analyser we noticed, on rotating the capillary with respect to the polarisation direction of the incident light, a distinct variation in intensity of the transmitted light (Fig. 3d-e and Supplementary Video 1), the maximum occurring when the capillary was perpendicular to the light polarisation. The effect reflects the anisotropic optical properties of the nanotubes, absorbing light polarised parallel to the nanotube axis but letting through light polarised perpendicular to the tube[21]. Because the nanotubes were now aligned along the director of the liquid crystal, which was aligned preferentially along the capillary axis, light was absorbed more efficiently when the capillary was oriented along the polarisation direction of the incident light. The effect is quantified in Fig. 3f, showing the transmittance of blue, green and red light as a function of the angle between the capillary axis and the polarisation direction of the incident light. As expected for a suspension of a natural SWCNT sample, containing a random mixture of chiralities and a certain spread of diameters, consequently absorbing light of any colour, the transmittance is basically independent of wavelength.

The phenomenon could also be seen with the naked eye by illuminating the sample with unpolarised light and observing the capillary through a linear polariser which was rotated around an axis perpendicular to the sample, *cf*. Fig. 3g-h. When taking these photos (presented in their entirety in Supplementary Fig. 1), the capillary with LC-dispersed CNTs was placed next to an identical capillary with HiPco SWCNTs dispersed at the same concentration in an isotropic SDBS+water solution, and one filled with a CNT-free CTAB+water hexagonal columnar LC phase. These two capillaries were unaffected by the rotation of the polariser, reflecting the random alignment and absence, respectively, of CNTs. In contrast, the LC-SWCNT sample was distinctly darker when the transmission direction of the polariser was along the capillary axis, since the LC-aligned SWCNTs have preferentially absorbed light with this polarisation direction. In effect, the LC-SWCNT sample thus acts as a self-assembled fluid achromatic linear polariser. The linear dichroism of carbon nanotubes has been observed in the same way on macroscopic scale once before by growing SWCNTs inside the columnar pores of a zeolite crystal[22], but this is the first time that a system displaying the phenomenon has been achieved via self-assembly and in a fluid state.

The observation demonstrates that the combination of LC and CNTs is potentially of interest for a new type of guest-host liquid crystal display (LCD)[23]. CNTs are both achromatic (assuming a natural mixture of chiralities) and long-term stable, in contrast to the monochrome organic dyes that today are used in guest-host LCDs. If a sufficient concentration of CNTs can be well dispersed in a thermotropic LC, this could thus be a route towards a polariser-free (and thus more energy-efficient) full-colour LCD. However, considerable materials development, either in functionalizing CNTs or in optimizing thermotropic LCs for the role of hosting CNTs, is called upon before the required CNT loading can be achieved in a liquid crystal suitable for display use.

From Fig. 3f we can extract the transmittance $T_{\|}$ for light polarised parallel to the director and $T_{\perp}$ for perpendicular polarisation, and then we can use the standard method for determining the nematic order parameter S of a liquid crystal doped with a dichroic dye[23] (in our case, the dye is the CNT):

$$S = \frac{D-1}{D+2} \qquad (1)$$

where $D = {}^{\log T_{\|}}\!\big/_{\log T_{\perp}}$ is called the dichroic ratio. This yields a fairly low value of $S \approx 0.3$ (perfect orientational order would give $S = 1$ while $S = 0$ corresponds to totally random orientation). Because the transmittance data have been obtained over a rather large area (circle with about 150 μm diameter) and because the director orientation exhibits non-negligible spatial fluctuations on a much smaller scale, as is obvious in the polarising microscopy textures in Fig. 3a and c, this low value is to be expected, mainly reflecting the imperfect alignment of the templating LC host. In addition, the ultrasonication procedure generally introduces defects and kinks in the SWCNTs, hence there may be a certain degree of 'intrinsic' orientational disorder simply because the CNTs are not perfectly straight.

The alignment of the nanotubes was confirmed also using polarised resonant Raman spectroscopy, *cf*. Fig. 4. In the upper row are the radial breathing mode (RBM), G-band and G'-band[21] regimes of the SWCNT response curves for polarisation parallel and perpendicular to the LC director, respectively, as obtained with a relatively large laser spot size (10 μm diameter). In the inset the G-band regime is displayed as obtained with an objective of higher magnification power, thus with a smaller spot size (2 μm diameter). While it is clear from the large difference in response for the two polarisations that the nanotubes are aligned preferentially along the LC director, it is also clear that the effective degree of order is somewhat higher when measuring with a smaller spot size, again reflecting the large-scale spatial variations of the LC director orientation.

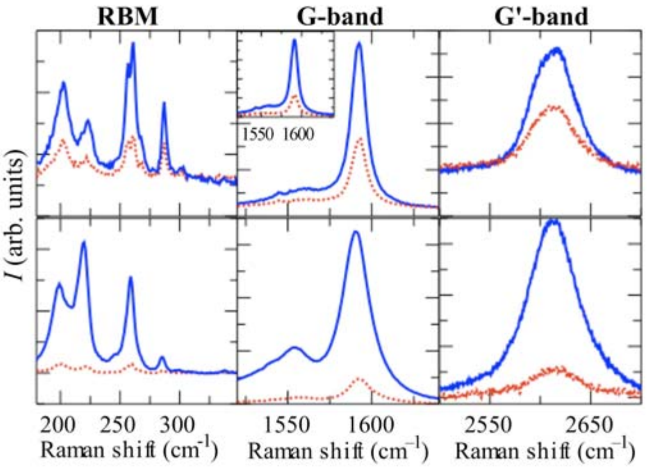


Fig. 4. Polarised Raman scattering intensity *I* of mixture **1** for excitation polarisation parallel (black, fully drawn lines) and perpendicular (grey, dotted lines) to the liquid crystal director, respectively, from the capillary sample (upper row; inset shows high-magnification response) and from a dried and rinsed filament (lower row).

Also from the Raman data we can get a quantitative value of the nematic order parameter for the CNTs— somewhat underestimated for the same reasons as for the value obtained from optical absorption data, discussed above—by using equation (1) under the assumption that the SWCNT Raman mode strengths are proportional to the absorbance $A = -\log T$ of the tubes, as described in our previous study[4]. For the data sets in Fig. 4 this yields the result $S \approx 0.3$ for the 10 μm beam spot (regardless of which peak is fitted), in agreement with the optical absorption data, but with the G-mode data obtained with 2 μm beam spot size, a value of $S \approx 0.6$ results. The difference clearly demonstrates the impact of imperfections in the large-scale sample alignment. As the LC alignment was not perfectly uniform even over the area of the smaller spot size, we can safely assume that the local CNT order parameter is higher yet. Indeed, with the quite large persistence length of SWCNTs (values of up to 1 μm have been suggested[24]) and with the relatively large degree of local orientational order inherent to the hexagonal columnar LC phase being the host, a higher degree of order should be expected. Later in this paper we describe how a sample with sufficiently good control of the macroscopic alignment can be achieved for this to be experimentally verified.

One might argue that the alignment of the CNTs is actually due just to the unidirectional flow of the viscous liquid hosting them while filling the capillary. That this is not the case can be seen in Fig. 5, showing optical microscopy pictures of a sample with small air bubbles. Around an air bubble the liquid crystal director field exhibits a quite complex pattern, as detected e.g. by viewing the sample between crossed polarisers (the optic axis is everywhere along the director) as in the top row. Clearly, there are several areas around the air bubble where the director is not along the filling direction. When removing the analyser (lower row), one sees that the absorption of light is maximally strong for polarisation along the director, not necessarily along the filling direction. As the absorption without analyser is due to the CNTs, this shows that the nanotubes are aligned along the liquid crystal director, whether it is along the flow direction or not. In fact, the orientation-dependent absorption in the lower row of Fig. 5 actually helps to determine the LC director field uniquely (indicated with thin bars in b and d), complementing the polarisation microscopy photos in the upper row in an informative way.

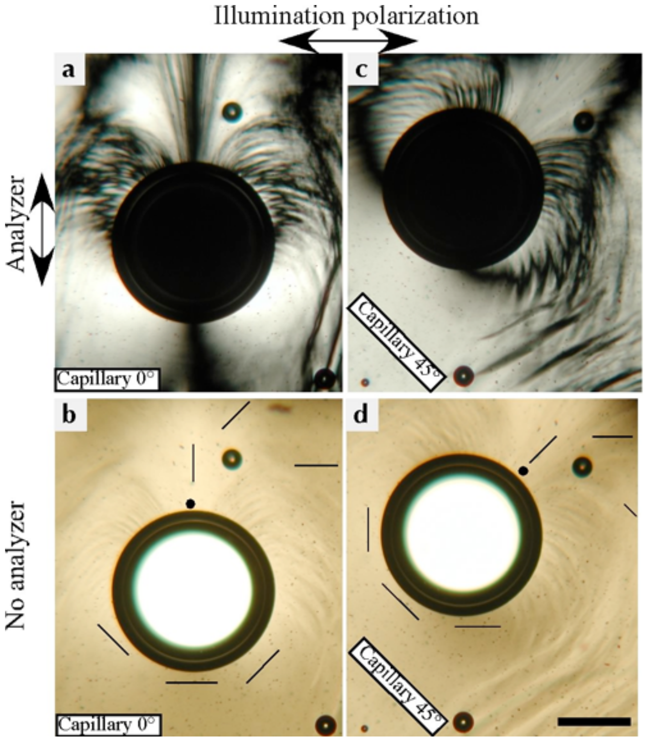


Fig. 5. The complex director pattern around an air bubble visualized between crossed polarisers (a and c). Removing the analyser (b and d), it is apparent that the light absorption pattern due to the SWCNTs follows the director pattern, demonstrating that the SWCNTs are aligned through LC templating, not by the flow during capillary filling. The thin bars in b and d indicate the director orientation in representative locations, as determined from the analysis of the textures. Scale bar (thick bar in d): 200 µm.

A very beneficial property of mixture **1** is that thin and highly aligned filaments easily can be drawn from it, as illustrated in Fig. 6. The filaments can be deposited on a substrate in any chosen direction (even with curvature) and multiple filaments can be crossed if desired, as illustrated in Fig. 6b with three filaments of different thicknesses. After deposition and fixation of the ends of the filaments, the substrate can be gently immersed in water to wash away the surfactant. Although some CNTs are also removed in the process, a considerable amount of nanotubes are left on the substrate, as evidenced by Raman spectroscopy, *cf*. the lower row in Fig. 3. The measurements were performed with polarisation parallel and perpendicular, respectively, to the direction along which the filament had been deposited. As is obvious from the spectra, the degree of SWCNT alignment along the filament was very good. The same method as used above for extracting the orientational order parameter now yielded a value of $S \approx 0.7$.

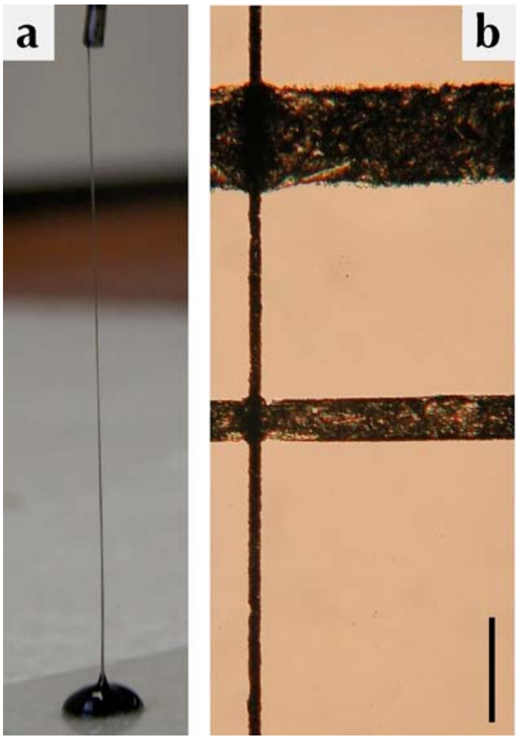


Fig. 6. Thin filaments can easily be pulled from the CNT-LC mixture (a) and deposited in any desired pattern on various substrates (b, scale bar 200 μm).

Conclusions and outlook

By combining ionic surfactants with opposite charge for dispersing unsupported carbon nanotubes and forming a lyotropic liquid crystal phase, respectively, we have achieved heavily loaded colloidal suspensions of CNTs which are spontaneously aligned along the director of the LC host. The anisotropic optical properties of the nanotubes are transferred to macroscopic scale by the LC, as evidenced by the liquid acting as a linear polarizer. The ability to pull thin filaments from the suspension gives us a very simple method to deposit the nanotubes onto arbitrary surfaces with control of the nanotube orientation. The water solubility of the surfactants allows us to subsequently rinse away the LC matrix. As the approach is very generic it can be employed to a variety of similar systems, varying both the guests and the host, with highly interesting results to be expected.

A most interesting extension to our work, which we are now pursuing, is to first fractionate the SWCNTs according to chirality, following methods that recently have been described in literature, using DNA[25] or sodium cholate[26] as surfactant. We will then be able to deposit e.g. only metallic SWCNTs, or semiconducting SWCNTs with well-defined band gap, along controlled directions on any substrate. Since no SWCNT growth method to date is selective regarding tube chirality, including those that allow control of tube direction, this would fill an important gap in current CNT processing methodology. It is also interesting to replace CTAB with a block-copolymer capable of forming a hexagonal LC phase, especially if the polymer is crosslinkable. This should be a promising route towards achieving composite materials with novel functionality or enhanced electrical, mechanical and / or thermal properties due to the presence of aligned CNTs at sufficient concentrations[27].

Experimental

(i) Samples and sample preparation

HiPco SWCNTs were purchased as “highly purified” (>95% SWCNTs according to manufacturer) from CNI Technologies and SDBS and CTAB from Sigma-Aldrich (80% and 99% purity, respectively). All were used as received. The SWCNTs were originally dispersed at a concentration of 5 mg/mL in an isotropic aqueous SDBS solution (SDBS to CNT mass ratio 5:1) using a Dr. Hielscher UP-200S ultrasound processor operating for 30 minutes on the sample, which was kept in an ice bath to avoid excessive heating. After this procedure, no CNT aggregation could be detected with optical microscopes. This suspension was diluted with water to obtain a CNT concentration of 2.5 mg/mL, whereafter the amount of CTAB required to form the LC phase was added as a dry powder, resulting in mixture **1**. A first homogenization of the mixture was achieved by rapid vortex mixing for about 2 minutes, whereafter it was placed in an ultrasound bath (Bransonic 32) for about 15 hours. Finally, just before filling a capillary or pulling filaments, the sample was again briefly tip-sonicated, this time with a lower-power ultrasound processor (Dr. Hielscher UP-50H), for 7 minutes. The optically flat glass capillary (Camlab, 200 μm thickness) was filled by means of the gentle vacuum suction generated by a syringe attached to the capillary via a small piece of rubber tubing, whereas the filaments were obtained simply by dipping a sharp tip, e.g. a syringe needle, into the mixture and moving it away.

(ii) Characterization

X-ray scattering experiments were performed with a Bruker AXS NanoSTAR (CuK_α radiation aligned by Goebel mirrors) equipped with a 2D-electronic detector and a temperature controller (MRI, Germany). Optical microscopy was carried out with Leica DMLP and Olympus BH-2 polarising microscopes. For optical transmittance measurements interference filters were used to monochromatise the incident light and a photo diode (FLC Electronics, Sweden) measured the transmitted intensity. As the reference sample required to get absolute transmittance values we used an identical capillary filled with the CNT-free reference mixture **2**, having the same composition of SDBS, CTAB and water as mixture **1**.

Raman spectroscopy experiments were carried out using a Jobin Yvon Labram Raman microscope in backscattering mode, with 633 nm wavelength excitation laser. The capillary was placed at 45° to the polarisation direction of the laser and the polarisation of the light hitting the sample was switched between parallel and perpendicular to the capillary axis by means of a λ/2-plate, the optic axis of which was oriented at ±22.5° angle from the incident laser polarisation.

Acknowledgments

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Legends for electronic supplementary information

Supplementary Fig. 1. Three capillaries filled with an isotropic SWCNT suspension, LC-aligned SWCNTs, and CNT-free LC, respectively (left to right), next to each other, underneath a linear polariser held with its transmission direction parallel (left photo) and perpendicular (right photo) to the capillary axes, respectively. Only the sample with LC-aligned SWCNTs changes its appearance, reflecting the alignment of the SWCNTs along the capillary axis.

Supplementary Video 1. Liquid crystal carbon nanotube polariser (movie file Video1.mov). Part 1: the LC-aligned SWCNTs in a 200 μm thick capillary observed in a microscope as it is illuminated by horizontally polarised light and slowly rotated. Part 2: the same capillary illuminated by unpolarised light and observed through a linear polariser which is rotated from transmission direction parallel to the capillary to perpendicular, and back.