

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

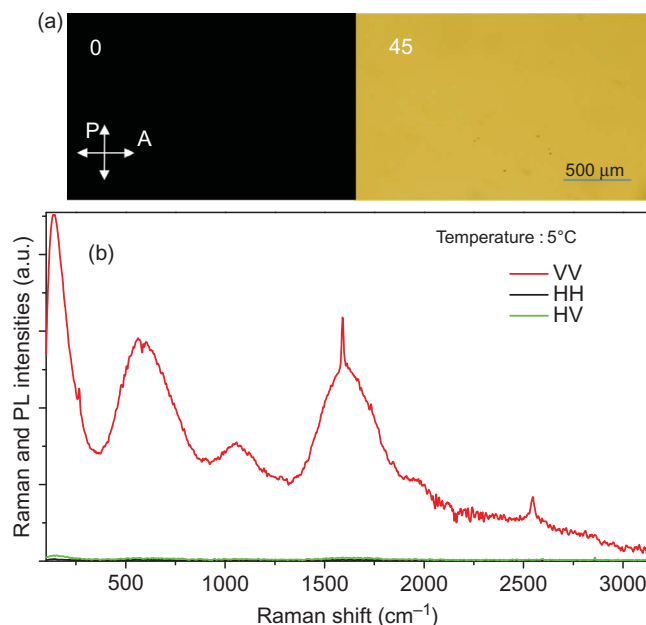


Figure 3. DNA/SWCNT suspensions in DSCG studied in a cell (6 μm) made by two parallel rubbed polyimide substrates. (a) Snapshots of cells observed by polarised optical microscopy at two different angles (0° left, 45° right) of the rubbing direction with respect to the polariser orientation. Also indicated 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

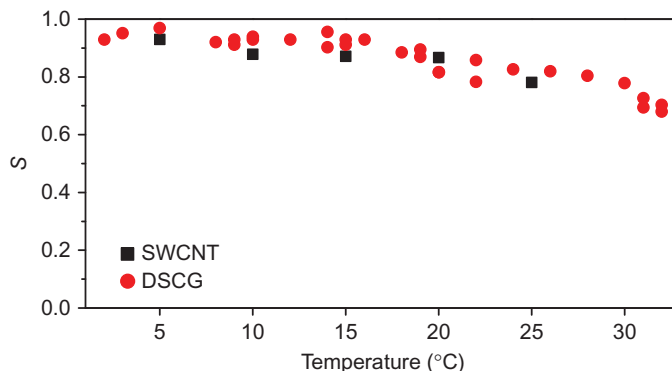


Figure 4. Order parameters of the DSCG (S^{LC}) and of the SWCNT (S^{CNT}) for the DNA/SWCNT suspension in DSCG obtained in a 6- μm thick cell with rubbed-polyimide alignment layers.

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.

References

- [1] Rao CNR, Govindaraj A. Carbon Nanotubes. In: O'Brien P, Kroto SH, FRS, Craighead H, editors. RSC nanoscience & nanotechnology: nanotubes and nanowires. 2nd ed. Cambridge: Royal Society of Chemistry; 2011. p. 18.
- [2] Byrne MT, Gun'ko YK. Recent advances in research on carbon nanotube-polymer composites. Adv Mat. 2010;22:1672–1688.

- [3] Ma P-C, Siddiqui NA, Marom G, Kim J-K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. *Compos Appl Sci Manuf*. 2010;41:1345–1367.
- [4] Russell JM, Oh S, LaRue I, Zhou O, Samulski ET. Alignment of nematic liquid crystals using carbon nanotube films. *Thin Solid Films*. 2006;509:53–57.
- [5] Miaudet P, Badaire S, Maugey M, Derré A, Pichot V, Launois P, Poulin P, Zakri C. Hot-drawing of single and multiwall carbon nanotube fibers for high toughness and alignment. *Nano Lett*. 2005;5:2212–2215.
- [6] Kim Y, Minami N, Kazaoui S. Highly polarized absorption and photoluminescence of stretch-aligned single-wall carbon nanotubes dispersed in gelatin films. *Appl Phys Lett*. 2005;86:73103–73107.
- [7] Ju SY, Kopcha WP, Papadimitrakopoulos F. Brightly fluorescent single-walled carbon nanotubes via an oxygen-excluding surfactant organization. *Science*. 2009;323:1319–1323.
- [8] Izard N, Kazaoui S, Hata K, Okazaki T, Saito T, Iijima S, Minami N. Semiconductor-enriched single wall carbon nanotube networks applied to field effect transistors. *Appl Phys Lett*. 2008;92:243112–243116.
- [9] Liu L, Ma W, Zhang Z. Macroscopic carbon nanotube assemblies: preparation, properties, and potential applications. *Small*. 2011;7:1504–1520.
- [10] Iakoubovskii K. Techniques of aligning carbon nanotubes. *Cent Eur J Phys*. 2009;7:645–653.
- [11] Ma YF, Wang B, Wu YP, Huang Y, Chen YS. The production of horizontally aligned single-walled carbon nanotubes. *Carbon*. 2011;49:4098–4110.
- [12] Yao Y, Xian X, Zhang J. Aligned, ultralong single-walled carbon nanotubes: from synthesis, sorting, to electronic devices. *Adv Mater*. 2010;22:2285–2310.
- [13] Druzhinina T, Hoepfner S, Schubert US. Strategies for post-synthesis alignment and immobilization of carbon nanotubes. *Adv Mater*. 2011;23:953–970.
- [14] Fujigaya T, Nakashima N. Methodology for homogeneous dispersion of single-walled carbon nanotubes by physical modification. *Polym J*. 2008;40:577–589.
- [15] Kim DS, Nepal D, Geckeler KE. Individualization of single-walled carbon nanotubes: is the solvent important? *Small*. 2005;1:1117–1124.
- [16] Wang H. Dispersing carbon nanotubes using surfactants. *Curr Opin Colloid Interface Sci*. 2009;14:364–371.
- [17] Etika KC, Cox MA, Grunlan JC. Tailored dispersion of carbon nanotubes in water with pH-responsive polymers. *Polymer*. 2010;51:1761–1770.
- [18] Badaire S, Zakri C, Maugey M, Derré A, Barisci JN, Wallace G, Poulin P. Liquid crystals of DNA-stabilized carbon nanotubes. *Adv Mater*. 2005;17:1673–1680.
- [19] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, Lu A, Iverson T, Shelimov K, Huffman CB, Rodriguez-Macias F, Shon YS, Lee TR, Colbert DT, Smalley RE. Fullerene pipes. *Science*. 1998;280:1253–1256.
- [20] Davis VA, Ericson LM, Parra-Vasquez ANG, Fan H, Wang Y, Prieto V, Longoria JA, Ramesh S, Saini RK, Kittrell C, Billups WE, Adams WW, Hauge RH, Smalley RE, Pasquali M. Phase behavior and rheology of SWNTs in superacids. *Macromolecules*. 2004;37:154–160.
- [21] Pénicaud A, Poulin P, Derré A, Anglaret E, Petit P. Spontaneous dissolution of a single-wall carbon nanotube salt. *J Am Chem Soc*. 2005;127:8–9.
- [22] Islam MF, Alsayed AM, Dogic Z, Zhang J, Lubensky TC, Yodh AG. Nematic nanotube gels. *Phys Rev Lett*. 2004;92:88303–88307.
- [23] Zamora-Ledezma C, Blanc C, Anglaret E. Controlled alignment of individual single-wall carbon nanotubes at high concentrations in polymer matrices. *J Phys Chem C*. 2012;116:13760–13766.
- [24] Islam MF, Milkie DE, Torrens ON, Yodh AG, Kikkawa JM. Magnetic heterogeneity and alignment of single wall carbon nanotubes. *Phys Rev B*. 2005;71:201401–201410.
- [25] Islam MF, Milkie DE, Kane CL, Yodh AG, Kikkawa JM. Direct measurement of the polarized optical absorption cross section of single-wall carbon nanotubes. *Phys Rev Lett*. 2004;93:37404–37408.
- [26] Zhang S, Kumar S. Carbon nanotubes as liquid crystals. *Small*. 2008;4:1270–1283.
- [27] Bisoyi HK, Kumar S. Carbon-based liquid crystals: art and science. *Liq Cryst*. 2011;38:1427–1449.
- [28] Kumar S, Bisoyi HK. Aligned carbon nanotubes in the supramolecular order of discotic liquid crystals. *Angew Chem*. 2007;46:1501–1503.
- [29] Dierking I, Casson K, Hampson R. Reorientation dynamics of liquid crystal-nanotube dispersions. *Jap J Appl Phys*. 2008;47:6390–6393.
- [30] Lagerwall J, Scalia G. Carbon nanotubes in liquid crystals. *J Mater Chem*. 2008;18:2890–2898.
- [31] Lagerwall J, Scalia G, Haluska M, Dettlaff-Weglikowska U, Roth S, Giesselmann F. Nanotube alignment using lyotropic liquid crystals. *Adv Mater*. 2007;19:359–370.
- [32] Scalia G. Alignment of carbon nanotubes in thermotropic and lyotropic liquid crystals. *Chem Phys Chem*. 2010;11:333–340.
- [33] Schymura S, Kühnast M, Lutz V, Jagiella S, Dettlaff-Weglikowska U, Roth S, Giesselmann F, Tschierske C, Scalia G, Lagerwall J. Towards efficient dispersion of carbon nanotubes in thermotropic liquid crystals. *Adv Funct Mater*. 2010;20:3350–3357.
- [34] van der Schoot P, Popa-Nita V, Kralj S. Alignment of carbon nanotubes in nematic liquid crystals. *J Phys Chem B*. 2008;112:4512–4518.
- [35] Maiti PK, Lansac Y, Glaser MA, Clark NA. Isodesmic self-assembly in lyotropic chromonic systems. *Liq Cryst*. 2002;29:619–626.
- [36] Lydon J. Chromonic liquid crystalline phases. *Liq Cryst*. 2011;38:1663–1681.
- [37] Liu H. Optical characterization of lyotropic chromonic liquid crystals. Kent (OH): Kent State University; 2006.
- [38] Zamora-Ledezma C, Blanc C, Maugey M, Zakri C, Poulin P, Anglaret E. Anisotropic thin films of single-wall carbon nanotubes from aligned lyotropic nematic suspensions. *Nano Lett*. 2008;8:4103–4107.
- [39] Zamora-Ledezma C, Blanc C, Anglaret E. Orientational order of single-wall carbon nanotubes in stretch-aligned photoluminescent composite films. *Phys Rev B*. 2009;80:113407–113420.
- [40] Johnson RR, Johnson ATC, Klein ML. Probing the structure of DNA-carbon nanotube hybrids with molecular dynamics. *Nano Lett*. 2008;8:69–75.
- [41] Simon KA, Sejwal P, Falcone ER, Burton EA, Yang S, Prashar D, Bandyopadhyay D, Narasimhan SK, Varghese N, Gobalasingham NS, Reese JB, Luk YY. Noncovalent polymerization and assembly in water promoted by thermodynamic incompatibility. *J Phys Chem B*. 2010;114:10357–10367.

- [42] Hartshor NH, Woodard GD. Mesomorphism in system disodium, chromoglycate-water. *Mol Cryst Liq Cryst.* 1973;23:343–368.
- [43] Hamodrakas S, Geddes AJ, Sheldrick B. X-ray analysis of disodium cromoglycate. *J Pharm Pharmac.* 1974;26:54–56.
- [44] Tortora L, Park HS, Kang SW, Savaryn V, Hong SH, Kaznatcheev K, Finotello D, Sprunt S, Kumar S, Lavrentovich OD. Self-assembly, condensation, and order in aqueous lyotropic chromonic liquid crystals crowded with additives. *Soft Matter.* 2010;6:4157–4167.
- [45] Nazarenko SVG, Boiko OP, Park H-S, Brodyn OM, Omelchenko MM, Tortora L, Nastishin Yu A, Lavrentovich OD. Surface alignment and anchoring transitions in nematic lyotropic chromonic liquid crystal. *Phys Rev Lett.* 2010;105:17801–17805.
- [46] O’Connell MJ, Bachilo SM, Huffman CB, Moore VC, Strano MS, Haroz EH, Rialon KL, Boul PJ, Noon WH, Kittrell C, Ma J, Hauge RH, Weisman RB, Smalley RE. Band gap fluorescence from individual single-walled carbon nanotubes. *Science.* 2002;297:593–596.
- [47] Bachilo SM, Strano MS, Kittrell C, Hauge RH, Smalley RE, Weisman RB. Structure-assigned optical spectra of single-walled carbon nanotubes. *Science.* 2002;298:2361–2366.
- [48] Nastishin YA, Liu H, Schneider T, Nazarenko V, Vasyuta R, Shiyanovskii SV, Lavrentovich OD. Optical characterization of the nematic lyotropic chromonic liquid crystals: light absorption, birefringence, and scalar order parameter. *Phys Rev E.* 2005;72:41711–41718.
- [49] Nastishin Yu A, Liu H, Shiyanovskii SV, Lavrentovich OD, Kostko AF, Anisimov MA. Pretransitional fluctuations in the isotropic phase of a lyotropic chromonic liquid crystal. *Phys Rev E.* 2004;70:51706–51714.
- [50] Goldfarb D, Luz Z, Spielberg N, Zimmermann H. Structural and orientational characteristics of the disodium cromoglycate-water mesophases by deuterium NMR and x-ray-diffraction. *Mol Cryst Liq Cryst.* 1985;126:225–246.
- [51] Lydon J. Chromonics. In: Demus D, Goodby J, Gray GW, Spiess HW, Vill V, editors. vol. 2B, *Handbook of liquid crystals.* Weinheim (Germany): Wiley-VCH; 1998.
- [52] Lucas A, Zakri C, Maugey M, Pasquali M, van der Schoot P, Poulin P. Kinetics of nanotube and microfiber scission under sonication. *J Phys Chem C.* 2009;113:20599–20605.
- [53] Puech N, Blanc Ch, Grelet E, Zamora-Ledezma C, Maugey M, Zakri C, Anglaret E, Poulin P. Highly ordered carbon nanotube nematic liquid crystals. *J Phys Chem C.* 2011;115:3272–3278.
- [54] Puech N, Dennison M, Blanc C, van der Schoot P, Dijkstra M, van Roij R, Poulin Ph, Grelet E. Orientational order of carbon nanotube guests in a nematic host suspension of colloidal viral rods. *Phys Rev Lett.* 2012;108:247801–247805.