DOI: 10.1002/anie.201203284

Hybrid Nanomaterials

# Discotic Ionic Liquid Crystals of Triphenylene as Dispersants for Orienting Single-Walled Carbon Nanotubes**

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A variety of soft electrical conductors have been developed by doping carbon nanotubes (CNTs) into organic and polymeric materials,[1] where better electrical properties are realized by dispersion of a larger amount of CNTs. Recently, liquid crystalline (LC) materials attract increasing attention for hybridization with CNTs,[2,3] as LC materials have the potential to orient CNTs for anisotropic electrical conduction. For example, CNTs have been shown to align in nematic LC mesophases of 4-cyano-4′-pentylbiphenyl and a mixture of alkyl- and alkoxycyanobiphenyls.[2a–c] However, the loading levels of CNTs are only as small as 0.01 wt%.[2g] Meanwhile, discotic LCs derived from triphenylene (TP) have been reported to orient CNTs.[3] However, owing to their rather low miscibility with pristine CNTs, the use of CNTs covalently modified with TP was essential. Herein we report that discotic ionic liquid crystals (ILCs) of TP derivatives $ILC_{col}$ and $ILC_{cub}$ (Figure 1a),[4,5] bearing six imidazolium ion pendants,[6] serve as excellent dispersants for pristine single-walled CNTs (SWNTs). The resultant composite materials can maintain their LC properties up to the SWNT content of about 8 wt%, which is 2–3 orders of magnitude greater than those reported previously. Of further interest, the ILC composites, when sheared, display anisotropic conducting properties,[7] as SWNTs are oriented along the shear direction. This orientation is kept for at least half a year.

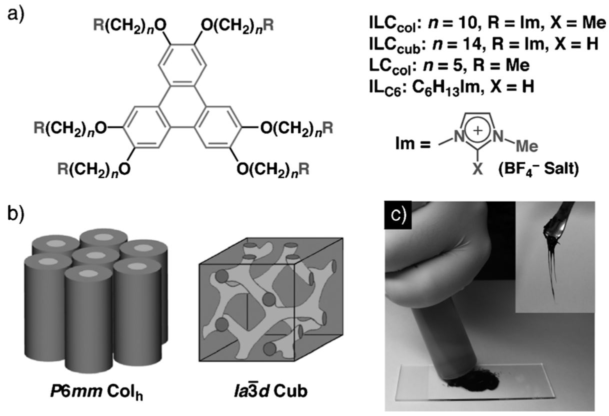


*Figure 1.* a) Molecular structures of ionic liquid crystals $ILC_{col}$ and $ILC_{cub}$, together with those of nonionic liquid crystal $LC_{col}$ and monovalent ionic liquid $IL_{C6}$ as references. b) Representations of the LC assemblies with hexagonal columnar and cubic geometries. c) Pictures of an $ILC_{col}$/SWNT composite.

In 2003, we reported that imidazolium ion-based ionic liquids (ILs), when being ground with SWNTs, are transformed into physical gels (bucky gels), where SWNTs are highly dispersed by a π-cation/π-electronic interaction and eventually form a 3D network structure associated with an interionic interaction of ILs.[6] As reported previously,[4,5] discotic ionic liquid crystals $ILC_{col}$ and $ILC_{cub}$ (Figure 1a) utilized for the present study assemble into hexagonal columnar ($Col_h$, 134–18 °C on cooling; Figure 2a) and cubic (Cub, 221–18 °C on cooling; Figure 2b) mesophases, respectively, over a wide temperature range, including room temperature.[5]

As a typical example of the hybridization of ILCs with SWNTs, pristine HiPco SWNTs were added at 150 °C to $ILC_{col}$ (isotropic melt) with a SWNT content of 5 wt%, and the mixture was ground with a pestle for 30 min (Figure 1c), whereupon it turned to a viscous black paste (Figure 1c, inset). As observed by optical microscopy (Figure 3a) and cross-section transmission electron microscopy (TEM, Figure 3b), only a very small amount of SWNT agglomerates was detected in the black paste. Similar black pastes resulted when

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[**] The synchrotron radiation experiments were performed at BL44B2 in SPring-8 with the approval of RIKEN (Proposal No. 20100024). This work was partly supported by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203284.

  

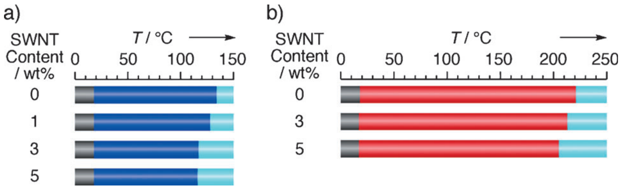


***Figure 2.*** Phase behaviors of a) $ILC_{col}$ and b) $ILC_{cub}$ and their composites with SWNTs determined from DSC traces on cooling from their isotropic melts. Gray: glass, blue: hexagonal columnar, red: cubic, light blue: isotropic melt.

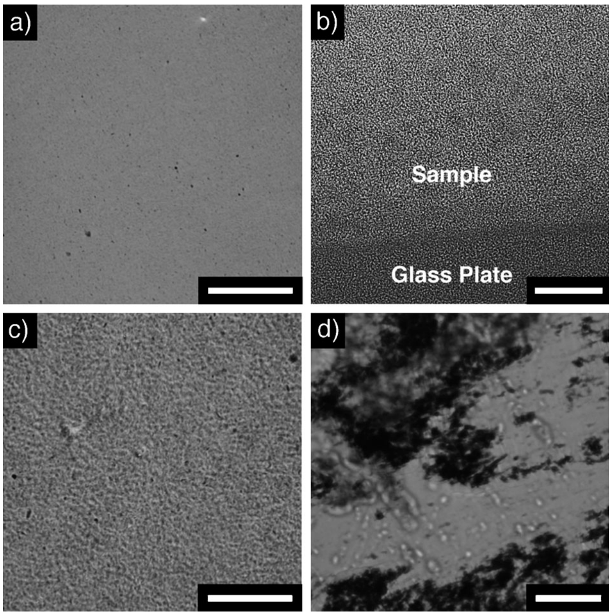


***Figure 3.*** a) Optical micrograph (25 °C) of an $ILC_{col}$ film doped with 5 wt% SWNTs on cooling from its isotropic melt at a rate of 1 °C min$^{-1}$. The sample was sandwiched by glass plates. Scale bar: 50 μm. b) High-resolution cross-section TEM micrographs of $ILC_{col}$ doped with 3 wt% SWNTs at the sample–glass interface. Scale bar: 10 nm. c, d) Optical micrographs of $ILC_{cub}$ (c; 25 °C) and $LC_{col}$ (d; 75 °C) films doped with 5 wt% SWNTs on cooling from their isotropic melts at a rate of 1 °C min$^{-1}$. The samples were sandwiched by glass plates. Scale bars: 50 μm (c) and 100 μm (d).

the SWNT contents employed were in a range of 3–15 wt%. However, upon further increase in the doping level to 30 wt%, the mixture lost its fluidity and became semi-solid. Although doped SWNTs affected the phase diagram of $ILC_{col}$ to a certain extent, the LC clearing temperature decreased only by 18 °C (134→116 °C) when $ILC_{col}$ was doped with even 5 wt% SWNTs (Figure 2a; Supporting Information, Figure S1a). Likewise, SWNTs dispersed very well in $ILC_{cub}$ (Figure 3c), where the resulting composite again showed only a marginal decrease in the LC clearing temperature (221→205 °C on 5 wt% SWNT doping; Figure 2b; Supporting Information, Figure S1b). Of interest, the effects of doped SWNTs on the X-ray diffraction (XRD) profiles of $ILC_{col}$ and $ILC_{cub}$ were essentially different from one another. In the case of $ILC_{cub}$, as the doping level of SWNTs was higher, the diffraction peaks shifted toward a lower 2θ region (Supporting Information, Figure S2b, inset).[8] In contrast, the diffraction peaks of $ILC_{col}$ hardly shifted upon increment of the content of SWNTs (Supporting Information, Figure S2a, inset). These contrasting observations indicate that $ILC_{cub}$ accommodates SWNTs into its cubic lattice, whereas $ILC_{col}$ prefers to maintain its original 2D hexagonal lattice without incorporating SWNTs.

In sharp contrast with ILCs carrying imidazolium ion pendants, nonionic $LC_{col}$ (Figure 1a) hardly dispersed SWNTs. For example, optical microscopy of a sample at 25 °C, prepared by grinding $LC_{col}$ with 5 wt% SWNTs at 100 °C (isotropic melt), clearly showed SWNT agglomerates (Figure 3d). The same was true even when the content of SWNTs was reduced to 1 wt%. A monovalent reference, such as 1-hexyl-3-methylimidazolium tetrafluoroborate ($IL_{C6}$, Figure 1a),[6] dispersed SWNTs but much less efficiently than ILCs having multiple imidazolium ion pendants, where SWNT agglomerates still remained even after $IL_{C6}$/SWNTs were ground for 30 min.

In the course of the above studies, we noticed that the discotic LC columns of $ILC_{col}$, upon being doped with SWNTs, align homeotropically with respect to the substrate surface. For a clear demonstration of this phenomenon, SWNT-doped $ILC_{col}$ was sandwiched by glass plates (sample thickness: 5–10 μm) and allowed to assemble into a LC mesophase by slow cooling (1 °C min$^{-1}$) from its isotropic melt. As shown in Figure 4a, polarized optical microscopy (POM) of $ILC_{col}$ alone at 25 °C displayed a birefringent texture in the entire view. In contrast, POM of the $ILC_{col}$/SWNT (5 wt%) composite exhibited a dark-field image entirely (Figure 4d). The dark image did not turn bright upon rotation of the sample to any angles on the instrument stage. However, when the upper glass plate was slid by about 5 mm to shear the material, a birefringent texture, parallel to the shear direction, appeared (Figure 4e). This texture was not observed when the sheared sample was rotated by 45 degrees in such a way that the shear and polarizing directions coincided with one another (Figure 4f), indicating that the LC columns in the sheared sample are oriented horizontally with respect to the substrate. Therefore, the dark-field image shown in Figure 4d is a consequence of the homeotropic columnar orientation of $ILC_{col}$. We found that the homeotropic orientation is more difficult, as the sample thickness is larger (Figure 5; Supporting Information, Figure S3). For example, with 1 wt% SWNTs, a 3 μm-thick LC film displayed a complete dark-field image in its whole area (Supporting Information, Figure S3a), but a 10 μm-thick LC composite was partially birefringent (Figure 4b). Nevertheless, when the SWNT content was increased to 3 wt%, even a 15 μm-thick film in POM displayed a dark-field image (Figure 4c).[9] Doping with SWNTs is therefore essential for the homeotropic orientation of $ILC_{col}$.

By means of electronic absorption spectroscopy, we compared SWNT (3 wt%)-doped $ILC_{col}$ at its isotropic melt (150 °C) with that composed of homeotropically oriented LC columns (100 °C). In either case, the absorption spectrum clearly showed van Hove transition peaks owing to exfoliated SWNTs (Supporting Information, Figure S4),[10] where the spectral profiles in terms of the intensity and shape at 150 and

  

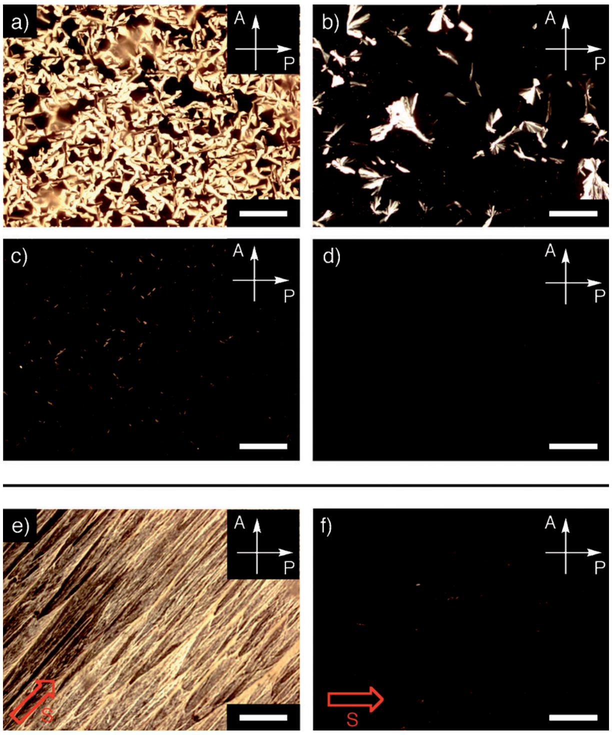


*Figure 4.* a)–d) POM micrographs (under crossed Nicols, 25 °C) of an unsheared $ILC_{col}$ film doped with a) 0, b) 1, c) 3, and d) 5 wt% SWNTs on cooling from their isotropic melts at a rate of 1 °C $min^{-1}$. The samples were 5 (a) and 10 μm (b–d) thick, and sandwiched by glass plates. e, f) POM micrographs (under crossed Nicols, 25 °C) of a sheared $ILC_{col}$ film doped with 5 wt% SWNTs. The sample was sheared at 100 °C. Arrows P, A, and S indicate the directions of polarizer, analyzer, and shear, respectively. Applied angles between the directions of polarizer and shear were 45 (e) and 0° (f). Scale bars: 100 μm.

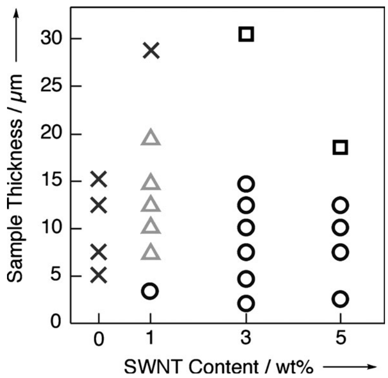


*Figure 5.* Levels of birefringence in POM at 25 °C as a function of film thickness, observed for $ILC_{col}$ films doped with 0, 1, 3, and 5 wt% SWNTs, sandwiched by glass plates. Symbols: ○ non-birefringent, △ partly birefringent, × entirely birefringent, □ optically non-transmittable.

100 °C were very similar to one another. Therefore, even when the LC columns of $ILC_{col}$ align homeotropically (100 °C), SWNTs are randomly oriented, just as they are in the isotropic melt. Then, what would be the role of SWNTs? As reported previously,[4] an interionic interaction among the imidazolium ion pendants of $ILC_{col}$ stabilizes its hexagonal columnar LC phase. However, when SWNTs are hybridized with $ILC_{col}$, the nanotubes are supposed to interact strongly with the imidazolium ion pendants, analogous to the case with imidazolium ion-based ILs,[6] thereby disturbing the nucleation event for the LC mesophase in the bulk. Note that $ILC_{col}$, just like imidazolium ion-based ILs, adhere strongly to a glass surface with a large hydrophilic nature. Consequently, the nucleation from the glass surface can occur preferentially, leading to the homeotropic growth of the columnar structure.

We found that a shear treatment of the ILC/SWNT composites induces a horizontal orientation of SWNTs with respect to the substrate surface (Figure 6; Supporting Information, Figures S5, S6). Typically, $ILC_{col}$ doped with 5 wt%

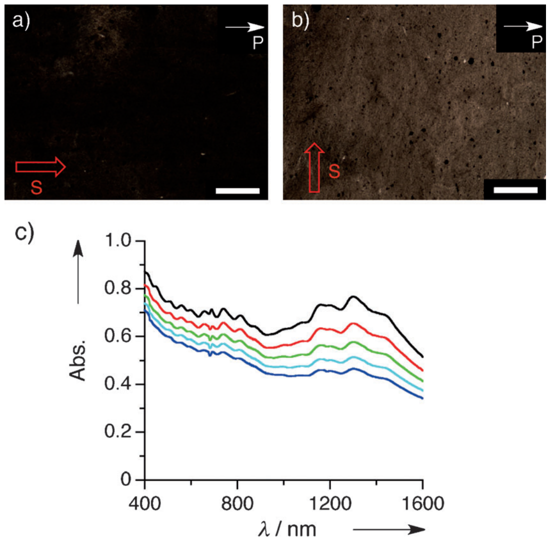


*Figure 6.* a, b) Optical microscopy texture (illuminated with polarized light, 25 °C) of a sheared $ILC_{col}$ film doped with 5 wt% SWNTs. The sample was sandwiched by quartz plates and sheared at 100 °C. Arrows P and S indicate the directions of polarizer and shear, respectively. Applied angles between the directions of polarizer and shear were a) 0 and b) 90°. Scale bars: 100 μm. c) Polarized absorption spectra (25 °C) of a sheared $ILC_{col}$ film doped with 5 wt% SWNTs. The sample was sandwiched by quartz plates and sheared at 100 °C. Applied angles between the directions of polarizer and shear were 0 (black), 30 (red), 45 (green), 60 (light blue), and 90° (blue).

SWNTs was sandwiched by glass plates and sheared at 100 °C. An optical microscopy texture, illuminated with polarized light, of the sheared composite was rather dark when the polarizing direction was parallel to the shear direction (Figure 6a).[2f] However, when the sample stage was rotated in such a way that the polarizing direction was orthogonal to the shear direction, the image turned much brighter (Figure 6b). Accordingly, polarized absorption spectroscopy of the composite showed that the spectral intensity changes with an applied angle between the polarizing and shear directions (Figure 6c). Without the shear treatment, the polarized absorption spectrum, in contrast, remained unchanged when the sample stage was rotated. As SWNTs bear a transition dipole along its longer axis,[11] these results clearly indicate that SWNTs in the sheared composite predominantly align along the shear direction. Noteworthy, neither nonionic $LC_{col}$

  

without imidazolium ion pendants nor monovalent ionic liquid $IL_{C6}$ (Figure 1 a) enabled such a shear-induced orientation of SWNTs (Supporting Information, Figures S7, S8).

As shown in Figure 7 a, when $ILC_{col}$ was used as the dispersion medium for SWNTs, shear in combination with annealing gave rise to three different states states 1–3 in terms of the orientations of the LC columns and SWNTs (POM; Supporting Information, Figure S9). Namely, the $ILC_{col}$/SWNT composite, upon shear treatment, gave state 1, where both LC columns and SWNTs were coaxially oriented horizontally with respect to the glass plates. Subsequent short annealing of the sheared composite for 5 min gave state 2, where the LC columns were oriented homeotropically while maintaining the horizontal orientation of SWNTs. Further annealing of the composite for 1 h gave state 3, where SWNTs were oriented randomly in the homeotropically oriented LC columns. The horizontal orientation of SWNTs, once generated by the shear treatment, was maintained for at least half a year at room temperature unless the material was heated. Namely, thermal reorientation of SWNTs occurs much less rapidly than that of the LC columns. As expected, when $ILC_{cub}$ was used as the dispersion medium for SWNTs, only two states, featuring horizontal and random orientations of SWNTs, were generated.

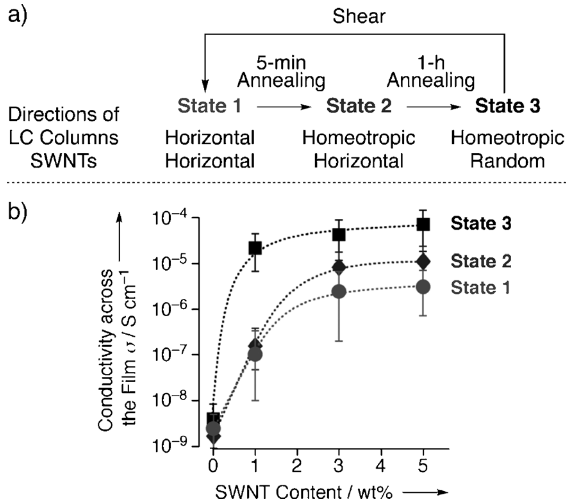


***Figure 7.*** a) Processing and orientational characteristics of states 1–3. $ILC_{col}$/SWNT composites were sheared (state 1), shortly annealed for 5 min at 150 °C (state 2), and then annealed for 1 h at 150 °C (state 3). b) Plots of conductivities across the film ($\sigma$) of states 1–3 at 25 °C of $ILC_{col}$ films doped with 0, 1, 3, and 5 wt % SWNTs, sandwiched by ITO electrodes with a separation of 12.5 μm.

Of particular interest, the orientation of SWNTs is a dominant factor for charge-carrier transport properties of the $ILC_{col}$/SWNT composite (Figure 7 b). For example, when $ILC_{col}$ doped with 1 wt % SWNTs was sandwiched by ITO electrodes, the DC conductivity $\sigma$ across the film at 25 °C in state 1 (circles) was nearly two orders of magnitude smaller than that in state 3 (squares). In contrast, state 1 and state 2 (rhomboids) were comparable to one another in DC conductivity, indicating a negligibly small contribution of the LC columns to the observed conduction profile. Meanwhile, at higher doping levels of SWNTs (3 and 5 wt %), the three states showed a much smaller difference (ca. 20 times) in their DC conductivities (Figure 7 b), which is possibly due to an enhanced probability of carrier hopping between SWNTs. In sharp contrast with the case of $ILC_{col}$/SWNTs, a SWNT composite with nonionic $LC_{col}$ containing non-dispersed SWNT agglomerates hardly showed a shear-induced electrical anisotropy (Supporting Information, Figure S10). We also investigated how effectively cubic $ILC_{cub}$ works for shear-induced anisotropic electrical conduction. As shown in the Supporting Information, Figure S11, the $\sigma$ values in state 3 were 3–4 times greater than those in state 1, indicating possible orientation of SWNTs. However, the extent of electrical anisotropy thus achieved was only one-fifth that of $ILC_{col}$/SWNTs under identical conditions. This result may be quite interesting, considering that $ILC_{cub}$, in contrast with $ILC_{col}$, accommodates SWNTs in its non-anisotropic cubic LC lattice (see above).

In conclusion, we have demonstrated that imidazolium ion-appended liquid crystalline (LC) triphenylene derivatives (Figure 1 a) are the best LC dispersants for pristine single-walled carbon nanotubes (SWNTs). Dispersed SWNTs, though randomly oriented in $ILC_{col}$, give rise to a homeotropic orientation of the LC columns up to a macroscopic length scale. Combination of shear and annealing treatments can give rise to three different states in terms of the orientations of the LC columns and SWNTs (Figure 7 a), where the anisotropy of electrical conduction is determined predominantly by whether SWNTs are oriented or not. The shear-induced orientation of SWNTs is maintained for a very long time (more than half a year) at room temperature.

Received: April 29, 2012
Revised: June 26, 2012
Published online: July 23, 2012

**Keywords:** carbon nanotubes · liquid crystals · electrical conduction · homeotropic orientation · ionic liquids

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[8] Provided that the cubic lattice of $ILC_{cub}$ isotropically expands when doped with SWNTs, the change in the XRD profile at the 5 wt% doping level, for example, corresponds to a 1.4% expansion of the lattice along each coordinate ($a=b=c=$ 94.7→96.0 Å).

[9] Film samples thicker than 15 μm suffered from an optical interference by SWNTs for POM evaluation.

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