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Carbon Nanotubes

Aligned Carbon Nanotubes in the Supramolecular Order of Discotic Liquid Crystals**

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The serendipitous discovery of carbon nanotubes (CNTs) by Iijima[1] in 1991 has generated tremendous activity in most areas of science and technology as a result of their unprecedented physical and chemical properties. CNTs, the one-dimensional carbon allotropes, are well-ordered all-carbon hollow cylinders of graphite with a high aspect ratio, which have a diameter of 0.4–2 nm for single-walled nanotubes (SWNTs) and 2–100 nm for coaxial multiwalled nanotubes (MWNTs) and lengths ranging from hundreds of nanometers to several micrometers. The combination of superlative mechanical, thermal, and electronic properties displayed by SWNTs and MWNTs make them ideal for a wide range of applications, such as conductive and high-strength composites, catalyst supports in heterogeneous catalysis, energy-storage and energy-conversion devices, field emitters, transistors, sensors, gas storage media, tips for scanning probe microscopy, and molecular wires. They are also of great interest in fundamental studies of electron transport in mesoscopic systems. A large number of biomedical applications of CNTs have also been envisaged. The synthesis, characterization, physical properties, and applications of CNTs have been extensively covered in several reviews.[2–8]

Despite the extraordinary promise of CNTs, their realistic application as one-dimensional conductors or semiconductors has been restricted because of difficulties in aligning them in the desired direction. Well-arrayed CNTs are highly desirable for the preparation of a variety of nanodevices, particularly where one-dimensional charge migration is important. There have been several attempts to develop well-aligned CNTs during growth by the chemical vapor deposition (CVD) process.[9,10] One of the earliest reported methods of aligning carbon MWNTs is based on cutting thin slices (50 to 200 nm) of a CNT–polymer composite.[11] The self-organizing properties of anisotropic, calamitic nematic liquid crystals have been exploited to align a minute number of CNTs and the composites have been studied for various properties.[12–16] On the basis of continuum-based density functional theory, it has been proposed that CNTs should form a columnar phase or a lyotropic liquid-crystalline phase in the presence and absence of van der Waals interactions.[17] Later, the formation of lyotropic liquid-crystalline phases by acid-functionalized CNTs in water,[18] DNA-stabilized CNTs in water,[19] and functionalized CNTs in acids[20] was reported. The integration of SWNTs in a hexagonal lyotropic liquid-crystalline phase of the well-known surfactant Triton X100 has recently been described by Weiss et al.,[21] and the preparation of nematic nanotube gels was reported by Islam et al.[22] A method of assembling SWNTs on functionalized patterned surfaces has also been proposed recently.[23] Hill et al. utilized a discotic amphiphilic hexabenzocoronene derivative to produce self-assembled graphitic nanotubes.[24] Herein, we present for the first time the functionalization of SWNTs with a discotic moiety and their alignment in the supramolecular order of a columnar mesophase.

SWNTs were purchased from CarboLex Inc. (Lexington, USA; AP grade) and were purified as reported.[25] The resultant carboxylic acid termini of the SWNTs were converted into acid chloride groups (SWNT-COCl) by treatment with thionyl chloride (see Scheme S1 in the Supporting Information). Hydroxy-terminated triphenylene was prepared by the etherification of monohydroxy-pentabutyloxy-triphenylene with 1-bromohexanol under classical reaction conditions and was fully characterized by spectral and elemental analysis.[26,27] Discotic-functionalized SWNTs were prepared by mixing SWNT-COCl with hydroxy-terminated triphenylene and heating the mixture at 80 °C for 48 h under anhydrous reaction conditions. The product was purified by column chromatography over silica gel. These functionalized SWNTs (f-SWNTs) were highly soluble in common organic solvents, such as dichloromethane, chloroform, and THF. The formation of discotic-functionalized SWNTs was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and thermogravimetric analysis (TGA).[27] The FTIR spectrum of discotic-functionalized SWNTs displays clearly the ester carbonyl stretching mode at 1737 cm^{-1} (Figure 1). The ^{1}H NMR signals are compatible with the successful covalent attachment of the triphenylene units to the SWNTs. The OCH_2 signal for hydroxy-terminated triphenylene shifts from $\delta = 3.6$ ppm to 4.1 ppm, which is expected for an ester functionality. The ^{13}C NMR results also support the functionalization of SWNTs. The signal at $\delta = 62.9$ ppm, which corresponds to the carbon connected to the OH group, shifts to $\delta = 68.9$ ppm for the carbon connected to the COO group. However, no carbonyl carbon signal was detected. This could be because of the very long relaxation times of the nanotube carbon atoms.[28] TGA displayed two partially overlapping peaks in the region 200–400 °C (approximately 60 % weight reduction), which may be attributed to the loss of triphenylene units. The high-temperature (450–650 °C) weight

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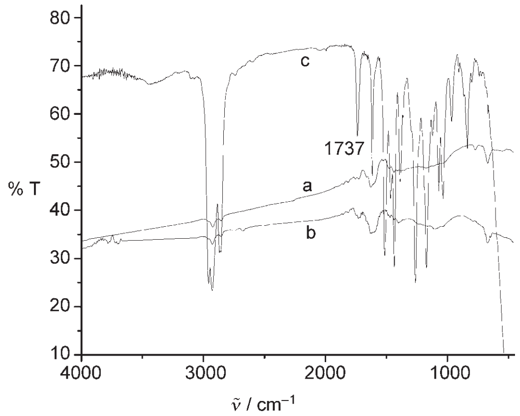

Figure 1. FTIR spectra of a) unfunctionalized, b) carboxyl-functionalized, and c) triphenylene-functionalized SWNTs.

loss of about 40% is most likely caused by the loss of SWNTs. The triphenylene-capped SWNTs were found to be non-liquid-crystalline. The waxy solid melts at about 40°C to form the isotropic phase.

Composites of f-SWNTs and triphenylene-based discotic liquid crystals (DLCs), namely, hexabutyloxytriphenylene (H4TP), were prepared by sonicating the two components in dichloromethane followed by removal of solvent and drying in a vacuum. Three compositions (by weight) of f-SWNTs–H4TP (**2a**: 2% f-SWNTs; **2b**: 5% f-SWNTs, and **2c**: 10% f-SWNTs) were prepared and analyzed by differential scanning calorimetry (DSC; Perkin–Elmer, Model Pyris 1D) and polarizing optical microscopy (POM; Olympus BX51 provided with a Mettler FP82HT heating stage and a Mettler FP90 central processor). All the f-SWNT–H4TP composites **2a–c** were found to be liquid-crystalline in nature. They show classical textures of the columnar mesophase upon cooling from the isotropic phase (Figure 2). Data obtained from the heating cycle of DSC are collected in Table 1. The DSC traces obtained on heating and cooling runs for pure H4TP and composite **2c** are shown in Figure S1 in the Supporting Information. The insertion of CNTs decreases the mesophase–isotropic phase transition temperatures significantly, but the crystal-to-mesophase transitions do not change much. This finding is logical, as the insertion of CNTs is expected to reduce the ordering of the cores. Similar effects have been observed on the insertion of gold nanoparticles into a discotic liquid-crystalline matrix.[29] At the moment, efforts have not been made, because of the paucity of the material, to find out the maximum amount of f-SWNTs that can be inserted in the DLC without destroying the columnar mesophase.

The X-ray diffraction patterns were recorded for composite **2c** and pure H4TP under the same conditions at 125°C. The X-ray data for H4TP were in agreement with the reported results.[30] The one-dimensional intensity versus 2θ profile for the composite **2c** is shown in Figure S2 in the Supporting Information. The overall features observed are consistent with the structure of the $\mathrm{Col_h}$ phase. Note that pure H4TP forms a more ordered $\mathrm{Col_p}$ phase,[30,31] which is characterized by three-dimensional crystal-like order in a hexagonal lattice, while the discs within the columns are able to rotate about the columnar axis. The insertion of SWNTs allows the positional freedom of discs, and thus all the composites display the classical $\mathrm{Col_h}$ phase. A significant shift of 0.8 nm in the reflection toward larger *d* spacing for the composite **2c** was observed. Pure H4TP exhibits reflections with a *d* spacing corresponding to 1.61 nm, while it was 2.39 nm in the case of composite **2c**. This clearly indicates the insertion of SWNTs in the supramolecular order of the columnar phase. A schematic representation of the insertion of SWNTs in the columnar mesophase is shown in Figure 3.

Figure 2. POM image of the columnar phase of **2c** at 130°C (crossed polarizers; 500× magnification).

Table 1: Phase-transition temperatures in the first heating scan of SWNT–DLC composites.

Composite	Thermal transitions [°C] (enthalpy changes [J g^{-1}]) [a]
H4TP	Cr 89 (37) $\mathrm{Col_p}$ 146 (31) I
2a	Cr 89 (37) $\mathrm{Col_h}$ 143 (23) I
2b	Cr 90 (35.4) $\mathrm{Col_h}$ 142 (19) I
2c	Cr 89.6 (30.6) $\mathrm{Col_h}$ 135 (11) I

[a] Cr = crystal, $\mathrm{Col_p}$ = columnar plastic phase, $\mathrm{Col_h}$ = hexagonal columnar mesophase, I = isotropic phase.

In conclusion, POM, DSC, and X-ray diffraction results indicate intercalation of SWNTs into the matrix of DLCs. The insertion of SWNTs causes a minor shift in the transition temperatures. The additional order of the $\mathrm{Col_p}$ phase is destroyed to give the normal $\mathrm{Col_h}$ phase. The significant shift of 0.8 nm in the reflection toward a larger *d* spacing is attributed to the integration of SWNTs in the hexagonal columnar phase along the director. These SWNT–DLC hybrid systems may be important for many device applications, such as photoconductors, light-emitting diodes, photo-

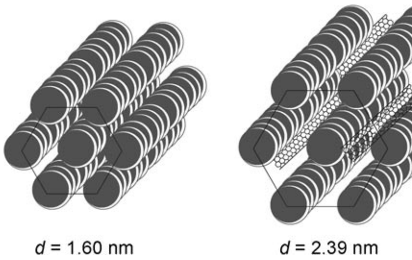

Figure 3. Schematic representation of the insertion of SWNTs in the supramolecular order of a columnar mesophase. The significant shift of about 0.8 nm in the reflection toward larger *d* spacing demonstrates the insertion of SWNTs in the hexagonal columnar phase.

voltaic solar cells, sensors, optical data storage, and thin-film transistors, as the dispersed SWNTs can be aligned in the desired direction using well-established liquid crystal alignment technologies.

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