# Carbon Nanotubes in Discotic Liquid Crystals

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Abstract | In this paper we have briefly reviewed the research on dispersion and alignment of carbon nanotubes in both thermotropic and lyotropic liquid crystalline phases. Formation of liquid crystalline phases of carbon nanotubes themselves and preparation of carbon nanotubes from discotic liquid crystals have also been discussed. Finally we have described our work on dispersion and alignment of functionalized carbon nanotubes in the columnar matrix of discotic liquid crystal monomers and polymers having electron rich and electron deficient cores exhibiting mesomorphism at room temperature.

## Introduction

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 fourth allotrope of carbon, after diamond, graphite and fullerene, are one dimensional, well ordered all-carbon hollow cylinders of graphite with a high aspect ratio. Generally CNTs are classified in two categories based on their structure and dimensions: single-walled carbon nanotubes (SWNT), which consist of one layer of cylindrical graphene and have diameters from 0.4–2.0 nm and lengths in the range 20–1000 nm; and multi-walled carbon nanotubes (MWNT), which contain several concentric graphene sheets and greater dimensions with diameters in the range of 1.4–100 nm and lengths from 1 to a few microns. Recent progress in synthesis has allowed the production of tubes with exactly two concentric carbon sheets, and hence the introduction of the concept of double-walled carbon nanotubes (DWNT).[2] SWNTs can be either metallic or semiconducting depending on the sheet direction about which the graphite sheet is rolled to form a nanotube cylinder. CNTs can be prepared by several methods, such as, chemical vapour deposition (CVD), carbon arc-discharge methods, high pressure carbon monoxide (HiPCO) method and laser ablation. These preparation methods yield random mixtures of tubes of various diameters, chirality, length distributions and different electronic properties.[3] All SWNTs and MWNTs are synthesized using catalysts, hence metal nanoparticles are likely to be present along with unwanted carbon particles such as graphite, amorphous carbon and non-tubular fullerenes. Carbon nanotubes are chemically extremely inert and practically insoluble. Strong van der Waals interactions between adjacent nanotubes promote clustering into crystalline ropes which in turn aggregate into strongly entangled and unorganized networks or bundles. Different protocols for post-growth CNT fractionation according to chirality and diameter have recently been described.[4] Different methods to separate semiconductive CNTs from conductive CNTs have been developed and exploited in their applications.[5] Synthetic strategies to chemically modify the side wall or tube-end by molecular or biomolecular components have been reported to obtain purified and soluble carbon nanotubes.[6] Other common techniques used to functionalize CNT are noncovalent exohedral with polymers and

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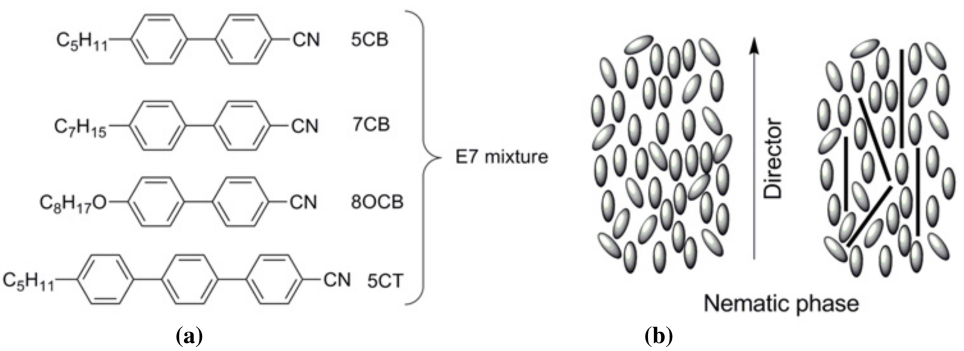
Figure 1: (a) is the commercial E7 mixture and (b) is the nematic phase of calamitic molecules which can align dispersed carbon nanotubes.



surfactants and endohedral functionalization with fullerenes, etc.[7] 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. A large number of biomedical applications of CNTs have also been envisaged and demonstrated.[8] The synthesis, characterization, physical properties and applications of CNTs have been extensively covered in several reviews.[9] 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. Recent studies have proved that the alignment of CNTs plays a critical role in the properties of nanotube based materials.[10] There have been several attempts to develop well-aligned CNTs during growth by the chemical vapor deposition (CVD) process.[11] One of the earliest reported methods of aligning MWNTs is based on cutting thin slices (50–200 nm) of a CNT–polymer composite.[12] Various other methods to align CNTs have been proposed by applying magnetic and electric field, shear flow or mechanical techniques. However, processing materials with well-controlled CNT alignment still remains a challenge.

Liquid crystals (LCs) are unique functional soft materials which possess both order and mobility at molecular and supramolecular level. LCs are currently an important phase of matter both scientifically and technologically. Liquid crystalline state—the fascinating, intriguing, beautiful, mysterious, delicate fourth state of matter, is an intermediate state between the solid and the liquid. Liquid crystal phases share some of the properties of both isotropic liquids and crystalline solids. While the molecules in these phases exhibit some positional and orientational order, they also behave as fluids. They combine both the fluidity of liquids and the anisotropy of crystals. The most common technological application of LCs is liquid crystal display (LCD). Apart from applications in the area of displays LCs are found in the field of surfactants and detergents, membranes, high strength polymers, photonics, thin films, semiconductors, artificial muscles, thermal, chemical and electrical sensors, etc.[13]

## CNTs in thermotropic liquid crystals

There has been growing interest in the field of dispersion of CNTs in both thermotropic and lyotropic liquid crystalline (LC) phases besides mesophase behavior of CNTs themselves and preparation of CNTs from discotic liquid crystals.[14] One of the most important applications of optoelectronic devices based on liquid crystals is liquid crystal display (LCD). To optimize the performance of a LCD, it usually requires prior knowledge of physical parameters of the LC mixture, such as the elastic constants of deformation, dielectric and optical anisotropies, conductivity and rotational viscosity. Mixing CNTs into thermotropic LC hosts has become one of the attempted approaches to modify the physical properties of LCs along with CNT alignment in LC matrix. LCs have the long range orientational order rendering them to be anisotropic phases. If CNTs can be well dispersed in LC matrix, they will in general align with their long axes along the LC director (Figure 1) to minimize distortions of the LC director field and thus the free energy. Dispersion of CNTs in LCs can provide us a cheap, simple, versatile and effective means of controlling nanotube orientation on macroscopic scale with no restrictions on nanotube type. The advantages of thermotropic LCs in this context are twofold. One, using existing alignment techniques, well developed for display industry, the ground state of the LC and hence of the dispersed CNTs can easily be determined on macroscopic scale. Second, the easy and speed of changing the director field by means of electric or magnetic fields can lead to switches based on reorientation of CNTs. The most commonly used thermotropic LCs for dispersing CNTs are E7 and 5CB which are shown in Figure 1. To our knowledge, the first report on doping of carbon nanotubes in liquid crystals is by Lee and Chiu in the year 2001 after one decade of CNTs discovery, who observed self-diffraction by gratings in nematic liquid crystals doped with multiwalled carbon nanotubes.[15] In the same year 2001, on the basis of continuum-based density functional theory, Somoza *et al.* proposed that CNTs should form a columnar phase or lyotropic liquid crystalline phase in the presence and absence of van der Waals interactions.[16] Subsequently, Lee *et al.* have observed efficient coherent light amplification with very high gains,[17] discovered the scenario pertaining to the surface-sustained permanent gratings[18] and strong beam coupling effects[19] in nematic liquid crystal and carbon nanotube mixtures. However, the work of Lynch and Patrick in 2002 caught the attention when they achieved high degree of CNT alignment along the nematic director field by taking the advantage of self-assembly properties of nematic liquid crystals and then removing the LC by vacuum suction leaving the CNTs alignment intact.[20] Khoo *et al.* have observed an extremely large electro-optically induced photorefractive effect in nematic liquid crystals doped with SWNTs and explained the basic mechanisms and conditions necessary for such nonlinearities.[21] It has been shown that doping with nanotubes can effectively reduce the dc driving voltage and improve the switching behavior of a twisted nematic-LC cell.[22] Voltage-dependent transmittance and capacitance under ac and dc electric field showed that the residual dc, which is related to an image sticking problem in liquid crystal displays, was greatly reduced due to the ion trapping by CNTs following strong charge transfer from the adjacent LC molecules.[23] Similarly under applied ac voltage the electro-optical properties of CNT doped TN-LCD cells are rectified by reducing the driving voltage and rise time.[24] Huang *et al.* have studied the electro-optical characteristics of twisted nematic (TN) mode and chiral homeotropic liquid crystal mode cells filled with +ve and –ve dielectric anisotropy liquid crystals doped with CNTs.[25] The improved electro-optical characteristics of the cells were attributed to the viscosity of the LC mixture. Comparison of SWNT and MWNT doped twisted nematic cells show that MWNTs are superior additives to SWNTs which is attributed to metallic character of MWNTs.[26] Local deformation of liquid crystal director induced by translational motion of carbon nanotubes under in-plane field was studied in a CNT-doped nematic LC cell.[27] The CNTs were well aligned with the LC director, when a critical ac field was applied, the CNTs began translational motion between the electrodes as a result of electrophoretic motion thereby causing deformation of local director field. Minute addition of carbon nanotubes suppress the undesired field screening effect and increases the charge mobilities in the presence of a strong field which is attributed to the parallel alignment of both the long axis of carbon nanotubes and the nematic director along the electric field.[28] The influence of CNTs on the elastic constant was studied and it was found that CNTs increase the effective elastic constant of the LC-CNT dispersions.[29] Rotational viscosity is the most practical physical parameter for designing a fast response LC device. It has been shown that rotational viscosity of the LC is decreased by doping the CNT additive.[30] The effect of CNTs on the electro-optical characteristic of the IPS (in-plain switching) mode is studied which shows that the effective retardation value of the CNTs-doped LC cell was reduced and its operation voltage was increased slightly compared with that in the pure LC cell.[31] Dierking *et al.* have studied the alignment and reorientation of doped carbon nanotubes in LC cells under both electric and magnetic fields along with the change in the conductivity of the LC cell upon reorientation of the CNTs with the liquid crystal director field.[32] Recently, they have also studied the reorientation dynamics of CNTs in liquid crystal medium.[33] Very interestingly, Cervini *et al.* have aligned MWNTs by a template assisted method using a homeotropically aligned liquid crystalline monomer that was subsequently polymerized to a rigid polymeric material which led to retention of the orientation of both the mesogens and more importantly the nanotube.[34] 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 concentration. Da Cruz *et al.* have dispersed SWNT in nematic LC, the materials were studied by X-ray scattering and observed unusual responses to magnetic fields.[35] Preparation of nanotube gel was reported by Islam *et al.*[36] Nematic elastomers with aligned carbon nanotubes exhibiting reversible infrared and electromechanical actuation,[37] and superelongation of carbon nanotube aggregates in liquid crystal medium[38] is also reported. The effect of carbon nanotubes on phase transitions of nematic liquid crystals and antiferroelectric chiral smectic liquid crystals are also reported.[39] In contrast to alignment of CNTs with liquid crystals, the alignment of liquid crystals has been achieved by CNTs.[40] Scalia *et al.* have studied the interaction between CNTs and liquid crystal molecules by Raman spectroscopy.[41] To understand the alignment of CNTs in LC medium and the dynamic response of CNTs under an external field, theoretical studies has been carried out to reveal the interaction between CNTs and LC by using density functional calculations. The study shows that there is a considerable charge transfer from LC molecule to the CNT which induces a permanent dipole moment on the CNT and this plays an important role for electro-optical responses of CNTs in the LC cells.[42]

## CNTs in Lyotropic liquid crystals

There are less examples of inclusion of carbon nanotubes into lyotropic liquid crystals. However, as lyotropic LCs are water based and common in biological and living systems, it could be very interesting to use CNT-lyotropic LC mixtures for biotechnological applications. Unfortunately, recent toxicological studies of CNTs indicate that CNTs could be as harmful as asbestos and, therefore, extensive studies are required before their *in vivo* medical application. In contrast to thermotropic LC-CNT composites, the lyotropic LC-CNT composites can be prepared in two different ways. One can start by preparing an isotropic low-surfactant-concentration suspension of CNTs and then that can be made liquid crystalline by adding more surfactant (Figure 2) or it can be added to an already prepared lyotropic liquid crystal sample. The insertion of CNTs into lyotropic liquid crystalline phases was first investigated in 2006 by Weiss *et al.*[43] They observed that both the *d*-spacing and viscosity of the hexagonal columnar phase increased with increase of carbon nanotube concentration. Subsequently, Lagerwall *et al.* have aligned carbon nanotubes in the lyotropic nematic liquid crystals formed by both rod shaped and disc shaped micelles.[44] Raman measurements indicated that the nanotubes are aligned along the LC director and allowed the determination of the order parameter. Jiang *et al.* have dispersed carbon nanotubes in a lyotropic liquid crystal formed in room-temperature ionic liquids.[45] As observed earlier, here also it was observed that the *d*-spacing as well as the viscosity of the medium was increased with increase in nanotube concentration. Recently, it was observed that CNTs incorporate into ordered lyotropic liquid crystalline phase while preserving the native *d*-spacing.[46] Very recently, Lagerwall *et al.* have combined cat- and anionic surfactants to form a liquid crystalline colloidal suspension of carbon nanotubes, which by virtue of the spontaneously formed hexagonal columnar LC structure are uniaxially aligned over macroscopic areas.[47] The nanotube concentration is so high that 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 to yield an unprecedented degree of control in the practical realization of carbon nanotube based devices and materials.

## Liquid crystal phases formed by CNTs

Carbon nanotubes can be viewed as highly anisometric rigid rod-like particles. Like other anisotropic and one dimensional molecules, CNTs can form lyotropic liquid crystalline phase. This research field has been developed by the groups of Windle, Poulin and Smalley. The basis for this phenomenon is the classical Onsager argument for liquid crystal phase formation in concentrated suspensions of rigid rods; if the aspect ratio of the rods and their concentration are both large enough the free energy of the system is reduced by forming a nematic phase.[48] Several experimental contributions have been reported, all of them describing different ways of making liquid crystalline phases of carbon nanotubes in solution. These systems form nematic phases via acid functionalization, acid protonation, gradual evaporation or absorption of amphiphilic molecules. The first report describing the nematic liquid crystalline phase behavior of MWNTs was in 2003 by Song *et al.*[49] Later this group studied in detail the isotropic–nematic transitions in dispersions of MWNTs.[50] They have also exploited the mesophase behavior of CNTs to separate short nanotubes from longer nanotubes which have strong tendency to form liquid crystalline phases.[51] Recently they have reported the size-dependence and elasticity of liquid crystalline multiwalled carbon nanotubes.[52] Lyotropic liquid crystalline phases of SWNT have been achieved by protonating the side walls of CNTs in strong acids.[53] The protonation of SWNTs sidewalls eliminate van der Walls interactions and promote the dispersion process, at higher concentrations SWNTs form nematic phases. Another approach to obtain liquid crystalline phase from unmodified SWNT is reported by Badaire *et al.*[54] They have dispersed CNTs by non-covalent wrapping of denatured DNA to CNTs which exhibit

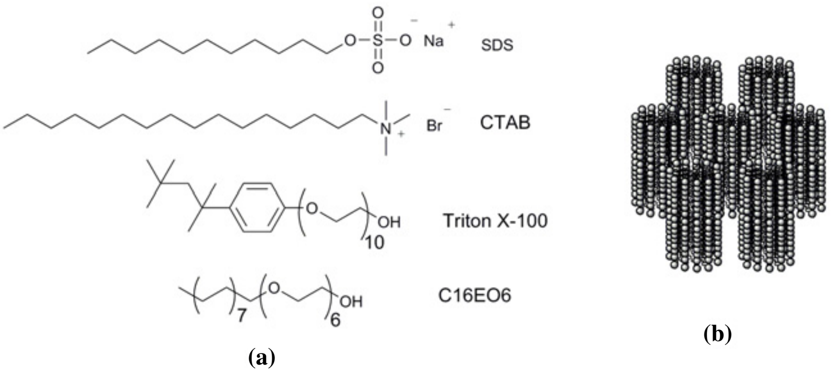


Figure 2: (a) represents the commonly used surfactants to disperse carbon nanotubes and (b) represents the columnar hexagonal liquid crystalline phase obtained from these surfactants in aqueous medium.

nematic phase but retains the intrinsic properties of CNTs. The liquid crystalline behavior of CNT solutions have been exploited to fabricate highly oriented carbon nanotube arrays for thin film transistors.[55] Liquid crystal behavior of SWNTs dispersed in biological hyaluronic acid solutions has been stabilized and studied.[56] Recently pyrene functionalized poly methyl methacrylate (PMMA) has been used for non-covalent functionalization of MWNTs which at high concentration self organize into ordered domains and hence exhibit liquid crystalline phase in PMMA as well as in PEG 400 matrices.[57] This offers the potential to align nanotubes at high volume fractions. While nematic phases have been experimentally reported, no evidence of smectic phases of carbon nanotubes has ever been shown. The observation of a smectic phase of rods necessitates a polydispersity as narrow as possible; the actual polydispersity of carbon nanotubes does not allow the formation of lamellar phases.

## Preparation of CNTs from discotic liquid crystals

Preparation of carbon nanotubes typically requires high temperature or high pressure. It is well known that in these cases the reactions are chemically complicated and difficult to control and one serious problem is the separation of the catalysts from the nanotube product as typically most of the catalyst particles are encapsulated into the nanotubes. Moreover, the orientation of the graphene layers in the nanotubes is important from their application point of view. To form ordered graphite nanostructures without metal catalysts and with desired graphene layer orientations, one possible approach is carbonization within a discotic columnar mesophase. From this point of view, the columnar super structures of discotic liquid crystals are worth precursors as the molecules possess a nano graphene subunit as the aromatic core and these molecules stack one on top the other to build up columns which in turn organize themselves in different two dimensional lattices (Figure 3). Upon carbonization under a controlled heating process the preorganized ordered columnar superstructures can be converted into nanotubes. Mullen *et al.* have produced nanotubes from thermotropic discotic liquid crystals[58] (Figure 4) whereas Crawford *et al.*[59] have produced nanotubes from both thermotropic and lyotropic discotic liquid crystals. Pyrolysis of well-defined discotic molecules in the bulk state produced novel carbon nano and microstructures. The temperatures are much lower than the normally used graphitization temperatures (2000–3000°C). Recently a template method has been used to fabricate uniform carbon nanotubes by pyrolysis of graphitic molecule hexabenzocoronene (HBC) in porous alumina membranes. Graphene molecules aligned along the channels and kept the order under slow heating procedures, after the template removal uniform carbon nanotubes with ordered graphene orientations were obtained in quantitative yield. Interestingly, the orientation of the graphene layers is perpendicular to the tube axis due to the preorganization of the disc-like molecules in the template. This is different from the case of normal carbon nanotubes, in which the graphene layers are parallel to the tube axis. Discotic molecules can also be converted into 1D carbon nanotube with well-controlled graphene layers orientation under template directed solid state pyrolysis process. Hill *et al.* have reported a unique approach to self-assembled graphitic nanotubes from an amphiphilic

Figure 3: Discotic molecules self-assemble one on top of the other to form columns and these so formed columns self-organize in two dimensional lattices, only columnar hexagonal structure is shown.

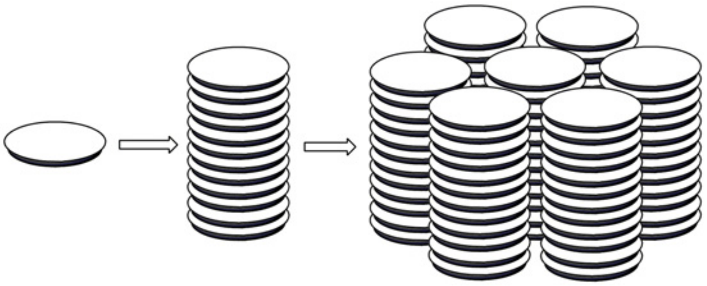
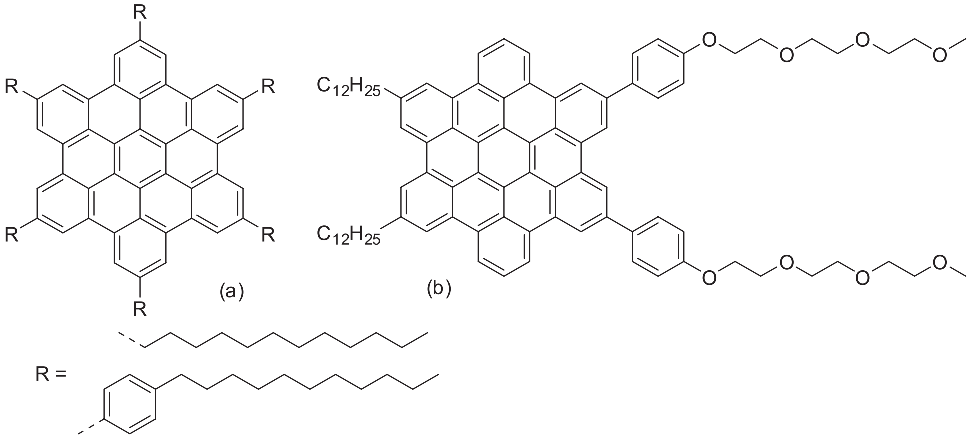


Figure 4: Precursor discotic molecules from which carbon nanotubes can be obtained via pyrolysis (a) or by dissolving in suitable solvent (b).

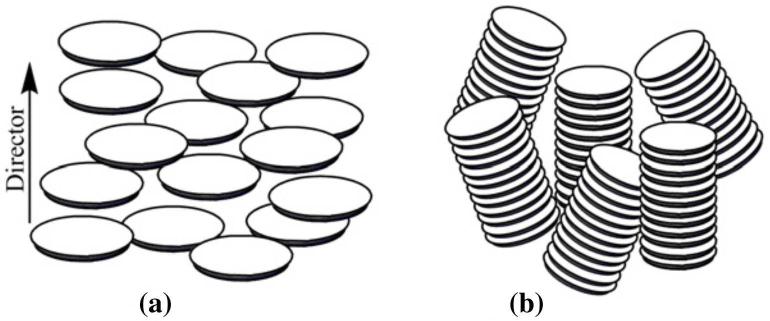


hexabenzocoronene (Figure 4).[60] In sharp contrast to the above nanotubes, their nanotubes consists of graphitic wall formed from numerous molecular graphene sheets stacked parallel to the longer axis of the tube. The proposed structure of the nanotube consists of helically rolled-up bilayer tapes composed of $\pi$-stacked HBC units, where the inner and outer HBC layers are connected by interdigitation of the hydrophobic alkyl chains while the hydrophilic ethylene oxide chains are located on both sides of the tubular wall. The $\pi$-stacked HBC units provide a charge carrier transport pathway. Suitable chemical modifications of the HBC amphiphile results in the formation of nanotubes with various interesting properties. Another interesting thing about these nanotubes is the formation of discotic columnar mesophase upon heating these graphitic nanotubes. Properties of liquid crystalline materials confined to restricted geometries are important from their potential applications point of view in electro-optics but imaging the molecular ordering in nanoscale confinements is very difficult. Recently Crawford *et al.* have obtained images of liquid crystalline ordering by covalently capturing discotic liquid crystals filled in multiwalled carbon nanotubes followed by carbonization. This shows face-on anchoring of the molecules due to strong $\pi$–$\pi$ interaction at the interface.[61]

## Discotic liquid crystals and their various phases

Since their discovery,[62] liquid crystals formed by disc-shaped molecules have been attracting growing interest because the supramolecular order of their columnar phases are of fundamental importance not only as models for the study of energy and charge migration in self-organized systems but also as functional materials for device applications such as one dimensional conductors, photoconductors,

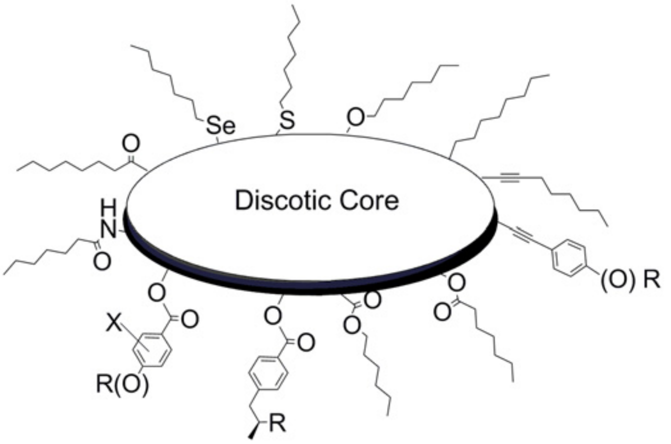
Figure 5: Nematic (a) and Columnar nematic (b) phases formed by discotic liquid crystals.



light emitting diodes, photovoltaic solar cells, field effect transistors and gas sensors. The functional capabilities of these materials are due to their easier processibility, spontaneous alignment between electrodes and self-healing of defects owing to their dynamic nature.[63] The negative birefringence films formed by polymerized nematic discotic liquid crystals have been commercialized as compensation foils to enlarge the viewing angle of commonly used twisted nematic liquid crystal display. To date the number of discotic liquid crystals derived from more than 50 different cores comes to about 3000. The hierarchical self-assembly of disc-shaped molecules leads to the formation of discotic liquid crystals. A majority of DLCs form columnar mesophases probably due to intense $\pi$–$\pi$ interactions of polyaromatic cores. The core–core (intracolumnar) separation in a columnar mesophase is usually of the order of 3.5 Å so that there is considerable overlap of $\pi$-orbitals. As flexible long aliphatic chains surround the core, the inter-columnar distance is usually 20–40 Å, depending on the lateral chain length. The number of aliphatic chains around the discotic core varies from 3–8 to produce columnar mesophase. Therefore, interactions between neighboring molecules within the same column would be much stronger than interactions between neighboring columns. Consequently, charge migration in these materials is expected to be quasi-one-dimensional. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction. Thus the columns may be described as molecular wires or more appropriately molecular cables since the conducting aromatic cores are surrounded by insulating aliphatic chains in the columnar phase.

Most of the discotics exhibit only one type of mesophase but a few examples with polymorphism are also known. Mesophases formed by disc-shaped molecules are primarily three types: (1) nematic, (2) columnar and (3) lamellar. The nematic phases of disc-shaped molecules can be subdivided into three types: (a) nematic discotic (b) chiral nematic and (c) columnar nematic. In the nematic discotic phase, the molecules stay more or less parallel, having orientational order but no long range positional order (Figure 5). The nematic phase of disc-shaped molecules is usually not miscible with the nematic phase of rod-shaped molecules. However, the symmetry of the nematic phase formed by disc-shaped molecules is identical to that formed by rod-shaped molecules. In discotic nematic phase the director is along the short molecular axes of the molecule since the disc normals are orientationally ordered. Like chiral calamitic nematic or cholesteric phase, chiral discotic nematic mesophase also exists. The mesophase occurs in mixtures of discotic nematic and mesomorphic or non-mesomorphic chiral dopants as well as in pure chiral discotic molecules. Chiral discotic nematic phase is characterized by a helical structure. The nematic columnar phase is characterized by a columnar stacking of the molecules. However, these columns do not form two-dimensional lattice structures (Figure 5). They display a positional short-range order and an orientational long-range order. In columnar mesophases, molecules assemble themselves one on top of the other in columns which are packed parallel on a two-dimensional lattice (Figure 3). The molecules may be arranged in a regular ordered manner or aperiodically. Depending on the order in the molecular stacking in the columns and the two dimensional lattice symmetry of the column packing, the columnar mesophases may be classified six classes: (a) columnar hexagonal phase, (b) columnar rectangular phase, (c) columnar oblique phase, (d) columnar plastic phase, (e) columnar helical phase and (f) columnar lamellar phase. Columnar hexagonal phase is characterized

Figure 6: General template of a discotic liquid crystalline molecules, the number of substituents around the core varies from 3–8 and the central core can be benzene, naphthalene, triphenylene, hexabenzocoronene etc.



by a hexagonal packing of the self-assembled molecular columns. Hexagonal columnar phases are denoted by Col$_h$ where h stands for hexagonal. The columnar rectangular mesophase consists of the stacking of the aromatic cores of the molecules in columns surrounded by the disordered aliphatic chains and packed in a rectangular fashion. Columnar rectangular phase is denoted by Col$_r$. In the columnar oblique mesophase, the columns are arranged with an oblique unit cell. Columnar plastic phase, denoted as Col$_p$, is characterized by three-dimensional crystal-like order in a hexagonal lattice, while the discs within the columns are able to rotate about the column axis. The longitudinal and lateral displacements of the discs in the Col$_p$ phase are restricted. An exceptional mesophase structure with helical order has been demonstrated for a triphenylene derivative namely hexahexylthiotriphenylene (HHTT). In this so-called H phase helical columns develop which interdigitate in groups of three columnar stacks. A layered structure is known to exist for mesophases of certain discotic compounds. Such a columnar lamellar mesophase is denoted by Col$_L$.

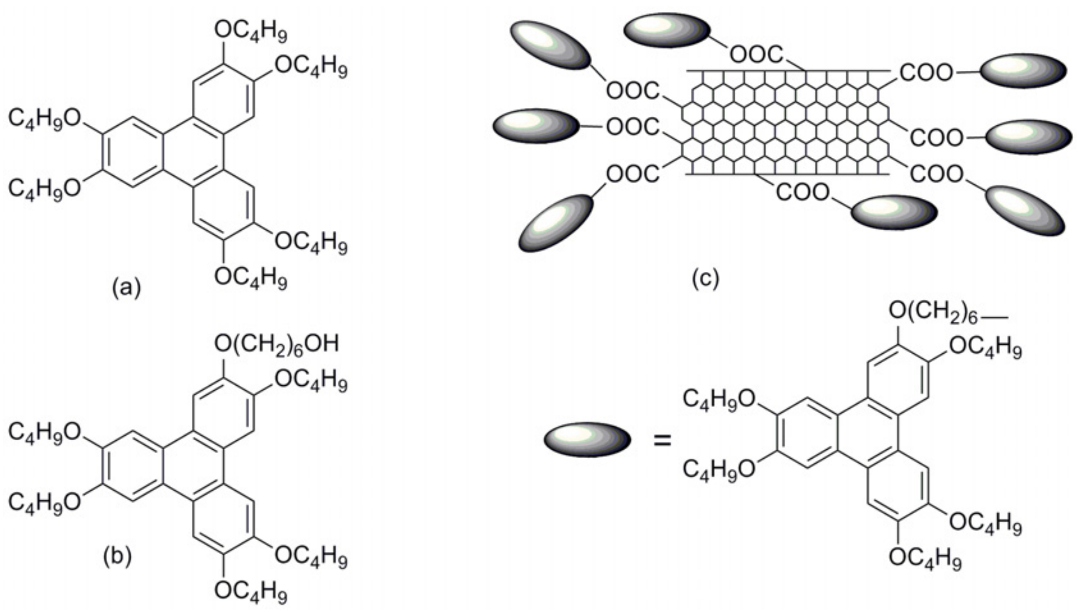
DLCs generally consist of flat, rigid aromatic cores surrounded by flexible chains. These materials often have two, three, four or six-fold symmetry and three or more peripheral chains of three or more carbon atoms. However, there are many exceptions and materials with low symmetry, with a non-planar, non-aromatic core having shorter number of chains are also documented. Flexible chains are connected to the core via different linking groups such as ether, ester, benzoate, alkyne etc. Figure 6 represents a general molecular architecture for discotic mesogens.

## CNTs in the supramolecular order of discotic liquid crystals

The insertion (dispersion) of CNTs in the supramolecular order of discotic liquid crystalline monomers and polymers may lead to novel materials with interesting properties useful for device applications. The ordered columnar phases, in contrast to isotropic and nematic phases, can offer wider opportunity for processing material with oriented nanotubes, a critical factor considering the strongly anisotropic properties of CNTs. Moreover, there are a lot of similarities between CNTs and discotic liquid crystals; first, both CNTs and DLCs are anisotropic materials. Second, both the materials posses self-assembling properties and often form hexagonal aggregates. Third and more important is the one dimensional (1D) conductivity properties of both CNTs and DLCs. Conductivity along the columnar axis of DLCs is several orders of magnitude greater than perpendicular to it, so also in CNTs, the conductivity along the CNT axis is much more higher than across the axis. Therefore, both the materials can be considered as "molecular wires". With this in mind, we have initiated a research program to disperse functionalized CNTs into the columnar matrix of liquid crystalline discotic monomers and polymers.[64]

At the beginning, we attempted to disperse acid-purified SWNTs into the columnar matrix of hexabutyloxy triphenylene (H4TP) in minute quantities but we observed that the purified CNTs form aggregates in the columnar phase which can be clearly seen under polarizing optical microscope (POM). It should be noticed that H4TP is a crystalline solid material at room temperature and

Figure 7: H4TP (a), hydroxyl functionalized H4TP derivative (b) and carton of discotic functionalized single walled carbon nanotube (c).



forms a highly ordered plastic columnar phase at high temperature.[65] Unlike the thermotropic calamitic nematic phase described above it fails to disperse purified CNTs adequately. Then we turned towards chemical functionalization of carbon nanotubes to make them compatible with the discotic liquid crystal matrix. The acid-purified and carboxylic acid-functionalized carbon nanotubes were chemically functionalized at the ends and sidewalls by a hydroxyl functionalized H4TP derivative (Figure 7). First the carboxylic acid groups of the CNTs were made more reactive by converting them into acid chlorides followed by esterification with the hydroxyl functionalized H4TP derivative to furnish discotic functionalized SWNTs (f-SWNTs) (Figure 8). These f-SWNTs were highly soluble in common organic solvents, such as dichloromethane, chloroform and THF. The formation of discotic functionalized CNTs was confirmed by IR, $^{1}$HNMR and $^{13}$C NMR spectroscopy and thermogravimetric analysis (TGA). However, the triphenylene capped SWNTs were found to be non-liquid-crystalline. Composites (2%, 5% and 10% by weight) of f-SWNTs and hexabutyloxy triphenylene were prepared and their liquid crystalline properties were investigated by POM, differential scanning calorimetry (DSC) and X-ray Diffraction studies (XRD). They show classical texture of columnar phases on cooling from the isotropic liquid state and no aggregations of CNTs are observed. The insertion of CNTs decreases the mesophase to isotropic transition temperatures significantly but 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. The X-ray diffraction pattern of pure H4TP was compared with the 10 wt% composite. A significant shift in the first order reflection toward larger $d$-spacing clearly indicates the insertion of CNTs in the supramolecular order of the columnar phase. The functionalized CNTs occupy the space between the disc columns and are oriented parallel to the columnar axis (Figure 8). Such stable CNT-DLC hybrid systems may be important for many device applications, such as photoconductors, light-emitting diodes, photovoltaic solar cells, sensors and thin-film transistors as the dispersed CNTs can be aligned in the desired direction using well established liquid crystal alignment technologies (Figure 8).

We have also studied the dispersion of commercial octadecylamine (ODA) functionalized CNTs in the columnar phases of triphenylene and rufigallol based discotic monomers and polymers.[64] Both triphenylene and rufigallol derivatives are earlier known discotic liquid crystals which form columnar mesophases.[66] The chemical structures of the compounds used in this study are shown in Figure 9 and they exhibit columnar mesomorphism at room temperature as characterized by POM, DSC

Figure 8: Alignment of carbon nanotubes along the columnar axis (a), homeotropic alignment of columnar phase where the column axis is perpendicular to the substrate (b) and uniaxial planar alignment of columnar phase where the column axis lies parallel to the substrate.

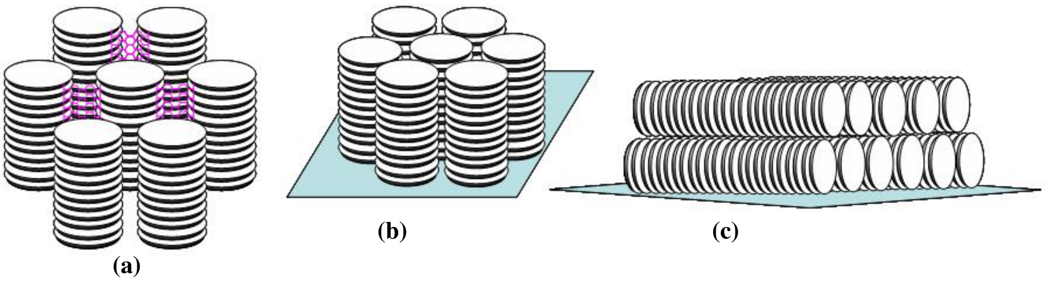
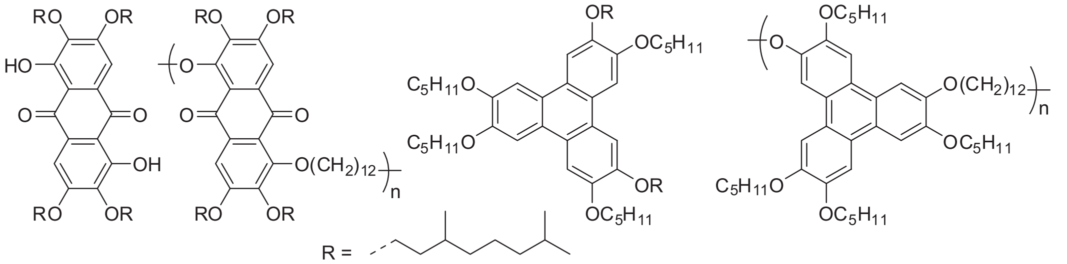


Figure 9: Room temperature discotic liquid crystalline rufigallol and triphenylene based discotic monomers and polymers.



and XRD studies. The soluble ODA functionalized CNTs in dichloromethane were added to the above monomers and polymers to prepared various CNT nanocomposites. Unlike discotic functionalized CNTs, here up to maximum of 2 wt% CNTs can be homogeneously dispersed. Beyond this percentage, small aggregates of CNTs can be observed under microscope. This study shows the importance of chemical compatibility of functionalized CNTs with the columnar phases. So, chemical functionalization of CNTs with mesogens should yield stable dispersions with high concentration of CNTs. The mesophase behaviors of the above dispersions reveal that with increase in CNT concentration the mesophase–isotropic transition temperatures decrease without disturbing the structure of the columnar mesophase of the host compounds. Though there is no significant change in the *d*-spacings of the composites compared to the pristine material, the high birefringence of the composites compared to the host material is indicative of CNT alignment along the columnar axis in the liquid crystalline matrix. These room-temperature liquid crystalline nanocomposites with broad mesophase ranges and different electronic properties may be important for many device applications.

## Conclusion

The studies of the properties of CNT based liquid crystals and CNT liquid crystal mixtures confirm that further and multidisciplinary research efforts are well worth in this field. Other functional materials and devices can be anticipated based on the intrinsic properties of CNTs such as their electronic properties for photovoltaic and field effect transistor applications in discotic liquid crystals and sensors with mats of ordered CNTs with enhanced properties compared to unoriented materials. The future of LC-CNT composites seems bright. A lot of theoretical work is still required to have better understanding of CNT and LC interactions. Mesogens should be designed to efficiently disperse CNTs in high concentrations into LC medium without compromising their intrinsic properties. The liquid crystal formation by CNTs themselves is also a highly interesting area which has already been used to spin fibers with well aligned CNTs. Research aiming to improve thermotropic LC properties by CNT addition must take great care to confirm that any observed effect is really due to the CNTs and not to impurities. There is no doubt that a significant part of nanoscience and nanotechnology will lie in the fourth state of matter containing the fourth form of carbon.

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