Supramolecular Nanocomposites: Dispersion of Zero-, One- and Two-dimensional Nanoparticles in Discotic Liquid Crystals

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Abstract. Discotic liquid crystals are emerging as novel nanomaterials useful in many device applications. Recently their hybridization with various zero-, one- and two-dimensional metallic and semiconducting nanoparticles has been realized to alter and improve their thermal, supramolecular and electronic properties. In this article, we have overviewed the work carried out in our laboratories on the dispersion of various metallic, semiconducting and carbon nanoparticles in discotic liquid crystals. First a brief introduction of self-organizing supramolecular liquid crystalline materials is presented with an emphasis on discotic liquid crystals. This is followed by the description of various discotic liquid crystal-nanoparticle hybrid systems. A number of discotic liquid crystals, functionalized nanoparticles and their nanocomposites were prepared and studied by spectroscopic and analytical tools. The dispersion of such functionalized nanomaterials in columnar matrix enhances the physical properties such as, conductivity, photoconductivity, absorbance, etc., significantly without disturbing the supramolecular properties.

1. Introduction

Supramolecular systems are formed from molecular systems with the help of many types of interactions, such as π–π interactions; dipolar and quadrupolar interactions; van der Waals interactions, charge transfer; hydrogen bonding and metal coordination. Supramolecular assemblies are extremely important in biological science; no life is possible without the self-assembly of lipid molecules into bilayers assembly within the cell membrane. Numerous Biosystems such as, DNA, collagen, enzymes, etc., are formed by the self-organization of small or large molecules using molecular recognition and supramolecular interactions [1]. Supramolecular assemblies formed due to non-covalent interactions in neat systems as well as in solvents are also very important in materials science. Clathrate compounds, host-guest complexes, molecular sieves, hydrogen-bonded complexes of guanidine, cyanuric acid, etc., are a few examples.

Liquid crystals (LCs) belong to one of such systems where supramolecular interactions play a crucial role in the formation of LCs and in the determination of their mesomorphic properties. Liquid crystalline state is a well-defined thermodynamically stable state of matter possessing the properties of both crystalline state and isotropic liquid state. Thus they combine both the order and mobility which is the basic principle for self-organization and structure formation in living systems. As the physical
properties of LCs fall in between those of the crystalline solid and amorphous liquid states, they are referred to as intermediate phases or mesophases. Some mesophases are very sensitive to small external forces, such as electric and magnetic fields, which is the basis for their application in information display. Many bio-molecules, such as carbohydrates, lipids, nucleic acids, have been found to exist in various liquid crystalline phases [2]. The formation of LC phases by nano DNAs (small fragment of DNA) indicates the significant role of LCs in the evolution of life in the prebiotic world [3].

LCs are ubiquitous in our present days life in the form of liquid crystal display devices (LCDs). Currently more numbers of LCDs exist than the people on earth. The LCDs industry is a multi-billion dollar industry. There are several other applications/potential applications of LCs such as, temperature-sensing (medical thermometers), solvent in chemical reactions, in chromatography, in spectroscopy, in holography, etc. Depending on how the mesophases are obtained, liquid-crystalline phases can be classified in two types, thermotropic and lyotropic. Lyotropic liquid-crystalline phases are obtained by mixing amphiphilic compounds in suitable solvents, quite often water, over a range of concentrations and temperatures. These are extremely important in biosciences. The thermotropic liquid-crystalline phases are obtained by heating a pure compound or a mixture of compounds or by cooling an isotropic liquid. LCs have also been classified as rod-like (calamitic) and disc-like (discotic), depending on the shape of the mesogenic molecules. This article deals only with the discotic liquid crystals.

The phenomena of liquid crystallinity in organic molecules was discovered in 1888 [4] and till 1977 all the mesogenic molecules reported were calamitic (rod-shaped). However, in 1977 a group of Indian scientists at the Raman Research Institute, Bangalore found that compounds with disc-like molecular shape are able to form liquid crystals [5]. They prepared some hexaesters of benzene (Figure. 1) and from optical, thermal and X-ray studies, it was confirmed that these materials form a new class of LCs in which molecules are stacked one on top of the other in columns and these molecular columns self-assemble in a hexagonal arrangement (Figure. 1).

![Figure 1](image.png)

*Figure 1.* Molecular structure of hexaalkanoyloxybenzene, the first DLC and its self-organization in the hexagonal columnar mesophase.

Discotic mesogens form primarily two types of mesophases; (i) nematic having only orientational order of molecules and (ii) columnar, having both orientational and positional order [6]. Both types of mesophases are very important for various device applications. Nematic DLCs can be polymerized to form negative birefringence films which have been commercialized as compensation foils to enlarge the viewing angle of commonly used LCDs [7,8]. They can also be used as active component in LCDs [8-10]. A majority of DLCs are derived from polycyclic aromatic cores having strong \( \pi - \pi \) interactions and, therefore, arrange themselves in columns. The separation in between two molecules (core–core separation) in a columnar mesophase is usually of the order of 3.5 Å. Therefore, there is considerable overlap of p-orbitals. As flexible long aliphatic chains surround the core, the separation between two columns (intercolumnar separation) is usually 20–40 Å, depending on the lateral chain length. Therefore, interactions between neighbouring molecules within the same column
are much stronger than interactions between neighbouring columns. Consequently, the migration of charge or energy in these materials is expected to be quasi one-dimensional. Accordingly, conductivity along the columns has been reported to be several orders of magnitude greater than in the perpendicular direction [11]. Therefore, the columnar mesophase may be described as molecular wires. Due to this unique property, DLCs have been extensively studied for the energy and charge migration and their device applications such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, field-effect transistors and gas sensors have been sought [12].

2. Nanomaterials
The past two decades have experienced an explosive development in the fields of nanostructured materials such as, metallic nanoparticles (NPs) and nanorods (NRs), semiconducting quantum dots (QDs), carbon nanotubes (CNTs), fullerenes and graphene. Materials that have at least one dimension in the range of 1–100 nm are defined as nanomaterials. These materials possess unique properties, which differ from those of bulk material and from individual atoms. For instance, when the size of metals decreases to one billionth of a meter, their conductivity decreases significantly and they become semiconductors; some metal NPs, but not bulk metal, possess antibacterial activity; the optical absorption (color) and fluorescence properties of metal NPs are very different than in the bulk materials [13, 14]. The nanoscience and nanotechnology have received great interest in nearly every field of science. The potential applications of nanomaterials in the fields of energy, computing, optics, catalysis, biosciences and medical sciences have been extensively discussed [15].

3. Liquid crystal nanoscience
Liquid crystals are organic nanoparticles usually in the range of 2-6 nm. Like nanomaterials, LCs also possess unique properties that differ from those of either crystals or liquids. Due to the emergence of this strong link between nanoscience and LCs, a new term, ‘Liquid Crystal Nanoscience,’ has evolved [16, 17]. Assembling metallic, semiconducting or carbon NPs into hierarchical self-assembling structures is a fascinating way to prepare advanced functional materials. The synergetic relationship of LCs possessing order and mobility at the molecular and supramolecular levels with the excellent electronic properties of various zero-dimensional (0-D), one-dimensional (1-D) and two-dimensional (2-D) metallic, semiconducting and carbon NPs may produce advanced functional materials for next generation electronic and opto-electronic applications [18-20]. Efforts have been made to alter the physical properties of LCs and NPs either by attaching liquid crystalline molecules covalently to NPs or by adding a low concentration of NPs to a liquid crystalline matrix. In the following sections, we will present an overview of our work on the dispersion of various functionalized NPs in DLCs.

4. Zero-dimensional nanoparticles in discotic liquid crystals
A three dimensional object when reduces to nanometer regime, is classified as zero-dimensional (0-D) object. Thus, NPs having all dimensions below100 nm are referred to as 0-D NPs. We have recently looked the dispersion of spherical 0-D GNPs (GNPs), CdSe and CdTe QDs in DLCs.

4.1. Spherical gold nanoparticles
The existence of GNPs is known since ancient times. However, the scientific evaluation of colloidal gold started by the classical work of Michael Faraday in 1857 [21]. With the availability of commercial electron microscope to well characterize nano-sized objects in conjunction with the synthesis of stable monolayer protected GNPs [22], the field grown rapidly. The Brust–Schiffrin simple synthesis of monolayer protected GNPs in organic solvent reported in 1994 [22] is perhaps the most popular method for producing smaller gold particles. In this method, a strong reducing agent, e.g., sodium borohydride was used to reduce gold(III) salt in the presence of an alkanethiol capping agent to produce 1–3 nm GNPs. We followed this method to prepare simple hexanethiol-protected GNPs as well as discotic functionalized GNPs [23, 24]. The synthesis is shown in Scheme 1.
Scheme 1. Synthesis of alkane- and discotic-functionalized GNPs

Hexanethiolate-capped gold clusters of 1.6 nm core diameter with an average composition of \( \text{Au}_{140}\left[\text{S(CH}_2\text{)}_5\text{CH}_3\right]_{53} \) were prepared by reducing \( \text{HAuCl}_4 \) with \( \text{NaBH}_4 \) in presence of hexanethiol. These NPs were fully characterized and dispersed in three different DLCs namely hexaxylyltriphenylene (HHTT), hexapentyloxytriphenylene (HPT) and hexakis(4-nonylphenylethynyl)benzene (H9B) [23]. HHTT is known to exhibit a highly ordered helical phase in addition to a hexagonal columnar mesophase [25]; HPT exhibits an ordered hexagonal columnar phase [26] and H9B displays a discotic nematic phase [27]. A few binary mixtures of hexanethiolat-functionalized GNPs with various DLCs were prepared by mixing the two components in a volatile solvent (dichloromethane) followed by removal of solvent and drying the sample under vacuum. Though, GNPs could not be well dispersed (a phase segregation was observed) in discotic nematic sample, the columnar phases of HHTT and HPT could well disperse the NPs in their matrices. These nanocomposites were analyzed by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (XRD), and conductivity studies. From experimental observations, it is attributed that GNPs are dispersed in the columnar phase evenly with a possibility of the formation of self-assembled superlattices of GNPs in the helical phase of HHTT [28]. An increase in the conductivity of the system was observed due to the presence of GNPs in the matrix [23, 29]. We also observed a decrease in orientational order parameter (S) and an increase in relaxation time (\( \tau \)) for disc motion with GNPs in columnar phase [30]. We have also looked the dispersion of hexanethiolate-functionalized GNPs in a lyotropic liquid crystalline phase and measured the dimensions of the hexagonally ordered phases both with and without nanoparticles using SAXS. The results show that the GNPs are dispersed in between the columns, essentially retaining the column dimensions [31].

These initial experiments clearly indicated that small spherical small GNPs can be easily dispersed in the columnar matrix of DLCs in low concentration without disturbing their mesomorphism. To look the effects of peripheral substitution on the GNPs, we designed GNPs fully covered with triphenylene discotic mesogens. Such a functionalization may yield liquid-crystalline GNPs or may have better compatibility with discotic host [24]. Thus, reduction of \( \text{HAuCl}_4 \) in the presence of thiol-functionalised triphenylene derivative yields discotic decorated GNPs (Scheme 1). These triphenylene-functionalised GNPs self-assemble into hexagonal patterns on the surface. This could be due to the strong \( \pi-\pi \) interactions between the triphenylene ligands of adjacent NPs. Shen et al. have also reported similar self-assembly of triphenylene covered GNPs on surfaces [32]. These discotic-functionalised GNPs could be easily dispersed in large quantities into the columnar phase of a related triphenylene DLC namely hexaheptyloxy-triphenylene (H7TP), owing to their chemical compatibility with one another. Remarkably, DC conductivity measurements show an enhancement of electrical conductivity by six orders of magnitude (Figure 2) under ambient conditions upon doping a very small amount (1%) of discotic-functionalized GNPs. We believe that GNPs are randomly dispersed in the columnar mesophase (Figure 2) and the enhancement in the conductivity could be due to the formation of charge transfer complexes between electron deficient NPs and electron rich DLC.
Figure 2. DC conductivity values as a function of temperature for 1% TPGNPs mixed with H7TP and neat H7TP and representation of the dispersion of NPs in a columnar metrics.

Later, similar observations were made by Holt et al.[33]. They also observed six orders of magnitude enhancement in electrical conductivity in the hexagonal columnar phase of a triphenylene-based DLC upon doping with methylbenzene thiol-covered GNP [33]. The enhancement in conductivity due to formation of small chain-like aggregates of GNP was proposed. These observations are highly significant from device application point of view. Further studies on structure–property relationship are desirable to fully understand the mechanism of charge migration in these nanocomposites and to further explore their potential applications.

4.2. Quantum dots in discotic liquid crystals

Quantum dots (QDs) are zero-dimensional semiconductor inorganic NPs. They have been extensively studied in recent times due to their potential applications in the life sciences and materials science [34-37]. We looked the dispersion of CdSe and CdTe QDs in DLCs [38,39]. These QDs were prepared as reported [40, 41] with some minor modifications and characterized by transmission electron microscopy (TEM), UV-Vis spectroscopy and photoluminescence spectroscopy. The TEM results confirm the synthesis of spherical particles with uniform sizes and shapes. Nanocomposites of both CdSe and CdTe QDs with triphenylene DLCs were prepared by mixing two components in chloroform under sonication followed by vacuum drying. These nanocomposites were studied by polarized optical microscopy, differential scanning calorimetry, X-ray and DC conductivity. Results were quite similar to GNP dispersion in DLCs. The dispersion of both CdSe and CdTe quantum dots in DLCs show higher conductivity compared to the pure compound. The doping of quantum dots into discotic liquid crystals does not disturb the nature of mesophase with different concentration variations but minor shift in the transition temperatures is observed. The enhanced conductivity makes QDs doped DLCs as potential candidates for various device applications such as, thin film transistors, LED’s, and organic solar cell.

Over all, it may be concluded that spherical metallic or semiconducting zero-dimensional NPs can be evenly distributed in the columnar matrix. The dispersion of NPs enhances the conductivity of the system up to six orders of magnitude under ambient conditions, making these nanocomposites suitable for application in many devices.
5. One-dimensional nanoparticles in discotic liquid crystals

Nanoparticles in which one dimension is out of the nanoscale while the others are in the nanoscale (1-100 nm), are termed as 1-D nanomaterials. These include nanotubes, nanorods, nanowires, etc. We have studied the dispersion of carbon nanotubes (CNTs) and gold nanorods (GNRs) in DLCs.

5.1. Carbon nanotubes in discotic liquid crystals

CNTs were discovered by Iijima in 1991 [42]. CNTs are all-carbon hollow cylinders of graphite with a high aspect ratio and are primarily two types; single-wall CNTs (SWNTs) which are formed by rolling a single sheet of graphene and, multi wall CNTs (MWNTs) formed by a few sheets of graphene. CNTs have been extensively studied due to their exciting electrical, mechanical and thermal properties [43-47]. Biomedical applications of CNTs have also been sought [48-50]. The functionalization of SWNTs with discotic molecules may generate liquid crystalline SWNTs, or will at least have better dispersibility in DLCs, with this idea, we functionalized SWNTs with triphenylene discotic mesogens [51]. Thus, acid-purified carboxylic acid-bearing SWNTs and hydroxyl-functionalized triphenylene derivatives were prepared and coupled via classical esterification reaction to yield discotic-functionalized SWNTs (f-SWNTs; Scheme 2). The product was well characterized by spectral, thermal and microscopic analyses. Nanocomposites of f-SWNTs and a DLC namely hexabutoxytriphenylene (H4TP) were prepared by mixing two components in dichloromethane under sonication followed by removal of solvent under vacuum. It is noteworthy that a very large amount (10%) of CNTs can be easily dispersed in DLC. This could be because of high compatibility of two systems. DLC-f-SWNTs nanocomposites were investigated using POM, differential scanning calorimetry and XRD. Results indicate insertion of the SWNTs in the supramolecular ordering of the columnar phase occupying the space between the disc columns (Scheme 2).

![Scheme 2. Synthesis of discotic-functionalized SWNTs and their dispersion in columnar matrix](image)

We have also studied the dispersion of non-discotic functionalized but processable simple octadecylamine-functionalized SWNTs in the columnar phases of triphenylene and rubigallol-based discotic monomers and polymers [52]. POM, DSC and XRD results indicate that these can also be dispersed in various discotic liquid crystalline monomers and polymers albeit in low concentration. Molecular compatibility of discotic-functionalized SWNTs due to π–π interactions of triphenylene molecules surrounding the SWNTs with the columnar phase forming triphenylene molecules likely stabilize the dispersion of f-SWNTs. Lee at al. dispersed pristine SWNTs in discotic ionic LCs derived from triphenylene core [53]. These nanocomposites exhibit anisotropic conducting properties.

5.2. Gold nanorods in columnar mesophase

The tunability of the surface plasmon band offers several applications of GNRs in bioscience and materials science [54, 55]. Unlike spherical GNPs, 1-D GNRs display two surface plasmon bands: a weak transverse band, similar to spherical GNPs, and a strong longitudinal band in the near-infrared region. The position of the longitudinal band red-shifts as the aspect ratio increases. GNRs with
different aspect ratios can be prepared via a number of methods. However, the seed-growth methods developed by Murphy [56] and El-Sayed [57] have received much attention because of their simplicity and high yield of well-defined monodispersed GNRs. Accordingly we prepared GNRs with an aspect ratio of 2.7 (about 15 nm wide and 40 nm long). These GNRs were passivated with dodecanethiol. Dispersion of GNRs in a triphenylene DLC namely, hexapentyloxy-triphenylene (HPT) was made by mixing dichloromethane solution of two components followed by removal of solvent. Thus, a number of composites were prepared and characterized by UV–Vis spectroscopy, POM, DSC, XRD and conductivity studies. Results indicate the alignment of GNRs along the columnar axis. The GNRs doped sample exhibits much higher conductivity than the undoped sample.

5.3. Gold nanorods embedded in discotic nanoribbons
When a solution of DLCs in a nonpolar solvent is treated with a polar solvent, discotic nanoribbons composed of discotic molecules with the \( \pi \) planes stacking in the direction of the long axis of the ribbon are formed. Xiao et al. reported that a hexabenzocoronene-based DLC organises into molecular stacks and that these stacks self-organise into cables or fibres [58]. Such nanoribbons have huge application potential in electronic devices. A field effect transistor was constructed using an isolated nanofiber. Discotic triphenylene, perylene and decacyclene molecules have also been used to develop nanowires which can be used for explosive sensing [59-61]. Metallic nanorods embedded discotic nanowires may provide better 1D conducting properties, with this idea, we looked into the formation of nanoribbons of undoped as well as GNRs doped triphenylene discotics. Thus a chloroform solution of HPT or HPT-GNR composites when treated with methanol, produces discotic nanoribbons. The dark field scanning transmission electron microscopy (STEM) image of 5% GNR-doped HPT nanoribbons (Figure 3) clearly demonstrate that in the nanoribbons formed by HPT-GNR composite, the GNRs are aligned with its long axis parallel to length of the ribbon.

**Figure 3.** SEM images of randomly oriented fibres of HPT (a); fibres formed by 1% GNR-HPT (b) and dark field STEM images of gold nanorods embedded in HPT nanoribbons (c). The bright spots in the fibres are due to gold nanorods embedded in the ribbon with their longitudinal axis parallel to length of ribbon [62].

Discotic molecules primarily self-assemble into columns; these columns then self-organize into hexagonal structures which grow into ribbon like structures. Similar treatment of DLC-GNR composites results in the formation of nanorods embedded discotic ribbons. These composites exhibit enhanced conductivity owing to insertion of metallic nanorods in ribbon like structures and, therefore, could be interesting materials for devices like field effect transistors.

6. Two-dimensional nanoparticles in columnar mesophase
A large number of DLCs are derived from polycyclic aromatic hydrocarbons (PAH) such as, benzene, triphenylene, coronene, etc. Graphene is the largest PAH. With its two-dimensional structure and fascinating physical properties, graphene has emerged as a potential candidate for various device applications [63-67]. In order to understand the effects of graphene dispersion in DLCs, we prepared
processable functionalized reduced graphene oxide. Graphene can be prepared via physical as well as chemical routes. The chemical route is more suitable for the preparation of a substantial amount of the materials. Oxidation of graphite following the Hummers method [68] produces graphene oxide (GO) with epoxy, hydroxyl and carboxyl groups. Carboxyl groups present at the edges are converted to more reactive acid chlorides which can be coupled with long chain amines. Thus, octadecylamine-functionalized graphene (f-graphene) was prepared as reported by Haddon et al. [69]. During the treatment of GO with thionyl chloride, to generate acid chloride groups, reduction of GO occurs, with some defects, and f-graphene is formed [70]. Formation of the desired f-graphene was confirmed by IR spectroscopy, elemental analysis, and X-ray diffraction. To disperse the functionalized graphene in DLC, a room temperature DLC namely 1,5-dihydroxy-2,3,6,7-tetrakis(3,7-dimethyloctyloxy)-9,10-anthraquinone (RTAQ) was prepared [71]. Dispersion of f-graphene in DLC was carried out by sonicating a dichloromethane solution of DLC and f-graphene for 30 min followed by removal of the solvent under vacuum. These DLC–graphene nanocomposites were analysed by UV-Vis spectroscopy, POM, DSC, XRD, Raman spectroscopy, elemental analysis, conductivity studies, SEM and cryo-SEM analysis [72]. Results indicate that graphene can be easily dispersed in low concentration in DLC without disturbing the parent mesophase. The doping of f-graphene stabilizes the discotic mesophase. This is due to enhanced local ordering of discotics on the surface of f-graphene owing to the π–π stacking between their aromatic cores. The Cryo-SEM images of composite having 1% of f-graphene in DLC (Figure 4) clearly show a layered structure unlike that of pure DLC. Layers observed in Cryo-SEM images of the composite are more ordered than those of f-graphene. Discotic molecules are arranged in the interlayer spacing of the f-graphene sheets. The system is stabilized due to π–π interaction between aromatic cores of graphene and discotic molecules. Upon closely observing the Cryo-SEM images of the composites, one can see domains of molecular columns present on f-graphene layers (Figure 4). Thus the system forms a “pillar-roof” type molecular building where discotic columns act as pillars and graphene as roof on these columns. The f-graphene-DLC composites show higher conductivity compared to pure DLC. The f-graphene layers act as bridges across defects resulting in more ordered mesophase and thus efficient charge transport. The creation of such mutually ordered sandwich like self-assembly of DLCs may widen the applicability of these nanocomposites in materials science.

![Figure 4](image_url)

**Figure 4.** (A) Cryo-SEM image of the composite also showing a layered structure and enlarged portion of (A) showing graphene layers covered by a layer of discotics (B) [72].

We have also looked the dispersion of graphene functionalized on the surface [73]. Thus, thiolated graphene oxide was prepared by reacting GO with various thiols. Thiophenol and hexadecanethiol are used separately for functionalization of GO. Nanocomposites were prepared by mixing two components in dichloromethane followed by vacuum drying. Nanocomposites were well characterized using POM, DSC, XRD, elemental analysis and SEM analysis. The results indicate that the dispersion of thiolated graphene in DLC causes destabilization of columnar mesophase. This could
be because of the functionalization of graphene on the surface which disturbed the efficient packing of discotic molecule in a columnar phase. However, the thiol-functionalized graphene samples self-assemble onto gold surface due to strong gold-thiol interactions. This monolayer film of graphene acting as blanket on the gold surface has potential application in various devices applications such as sensors, organic electronic devices etc.

7. Summary and outlook
The field of liquid crystal nanoscience is derived from two fascinating research fields; liquid crystals and nanoscience. Discotic nanoscience is a part of LC nanoscience involving only DLCs and NPs. It is emerged in the scientific literature very recently but has made significant advances during the past decade. A variety of DLC-NP hybrid systems have been realized and studied because of their interesting properties. These hybrid systems may find applications in a wide range of devices, including photovoltaic solar cells, thin film transistors, photoconductors and so on. DLCs have been covalently attached to various NPs. These discotic functionalized NPs as well as other functionalized NPs have been dispersed in DLCs. The zero-dimensional NPs are randomly dispersed in the columnar phase; one-dimensional NPs go along the columnar direction and the two-dimensional on the surface of columns. The dispersion of these NPs does not affect the mesomorphic properties significantly but improve physical properties significantly. For example, the electrical conductivity of the nanocomposites increases by several orders of magnitude compared with the pure discotic system. These nanocomposites may provide the next generation of advanced functional materials for many device applications.

8. References

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