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Discotic-Decorated Gold Nanoparticles

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Several mixtures of hexanethiolate capped gold nanoparticles and discotic liquid crystals were prepared. The thermophysical properties of these mixtures were investigated using polarizing optical microscopy, differential scanning calorimetry and DC conductivity. Formation of columnar mesophase and about 250 times enhancement in the DC conductivity indicate inclusion of gold nanoparticles into the matrix of triphenylene based discotic liquid crystals.

Keywords: columnar phase; discotic liquid crystals; gold nanoparticles; triphenylene

INTRODUCTION

There has been a growing interest in the fields of gold nanoparticles (GNPs) and discotic liquid crystals (DLCs) during the past decade. Although the reduction of gold salts to GNPs in solution is well known since Michael Faraday's seminal work in 19th century, the synthesis of monolayer-protected GNPs in organic solvents by Brust and co-workers [1] stimulated the research in this field significantly. More than 1300 reports have been appeared in the past decade on the chemistry and physics of organic-functionalized GNPs. Chemically functionalized GNPs can be handled like simple organic compounds [2]. They can be dried of solvents and redissolved without core aggregation. Classical chemical reactions can be performed on functionalized GNPs. As the physical properties of nano-sized metal particles are

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very different from those of bulk material, a number of potential applications of these nanoparticles have been envisaged [2,3].

The unique geometry of columnar mesophase formed by disc-shaped molecules, now commonly known as discotic liquid crystals [4], is of great importance to study the one-dimensional charge and energy migration in organized systems. There are a number of potential applications of these materials such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc. These interesting properties developed the synthesis of a large number of DLCs in recent years and currently more than 3300 compound of this category are known [5]. As the conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction, the columns may be described as molecular wire. Photoinduced charge carrier mobility in the range of $10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ to $0.71 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ has been reported in various columnar mesophases. Electroluminescence and photovoltaic devices based on DLCs have been prepared recently. Mechanism of charge transport and one-dimensional energy migration has also been studied extensively in these materials [6].

The intercalation of gold nanoparticles into a matrix of discotic liquid crystals may leads to novel composites with interesting properties useful for many device applications. With this in view, we have initiated a research program to incorporate gold nanoparticles in the supramolecular order of discotic liquid crystals by attaching DLCs covalently to the gold nanoparticles or by doping gold nanoparticles in DLCs. Preliminary results of our studies are reported here.

EXPERIMENTAL

GNPs covered with hexanethiolate monolayer **1** (Fig. 1) were prepared exactly following the reported method [7]. Thus, to a solution of tetraoctylammonium bromide (1.1 g) in toluene (65 ml) was added with stirring a solution of 158 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. This solution was stirred for 20 minutes and mixed with n-hexanethiol (142 mg) with further stirring for 10 minutes. To this mixture, a solution of 450 mg of NaBH_4 dissolved in 5 ml of water was added. The reaction mixture was stirred at room temperature for 24 hours. The organic phase was separated, evaporated to about 2–3 ml in a rotary evaporator under vacuum at room temperature, mixed with 50 ml ethanol and centrifuged at 5000 rpm for 1 hour. The supernatant liquid was removed. The resulting hexanethiol-protected gold nanoparticles were dissolved in about 1 ml of dichloromethane and precipitated with ethanol. The centrifugation and redispersal process was repeated several times to ensure

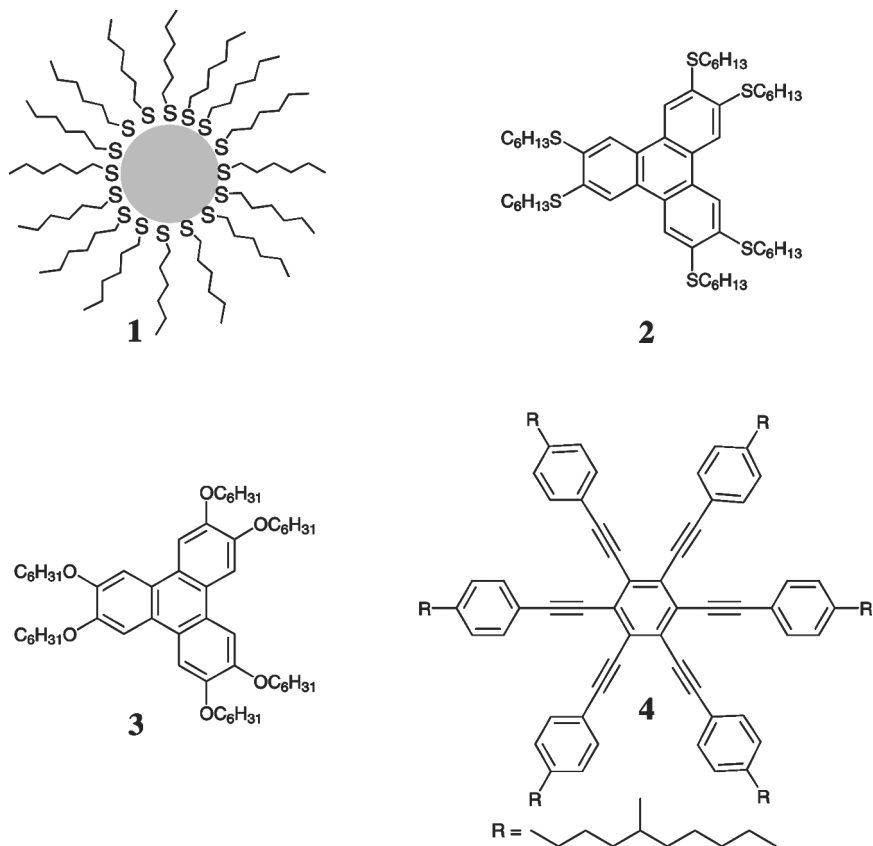
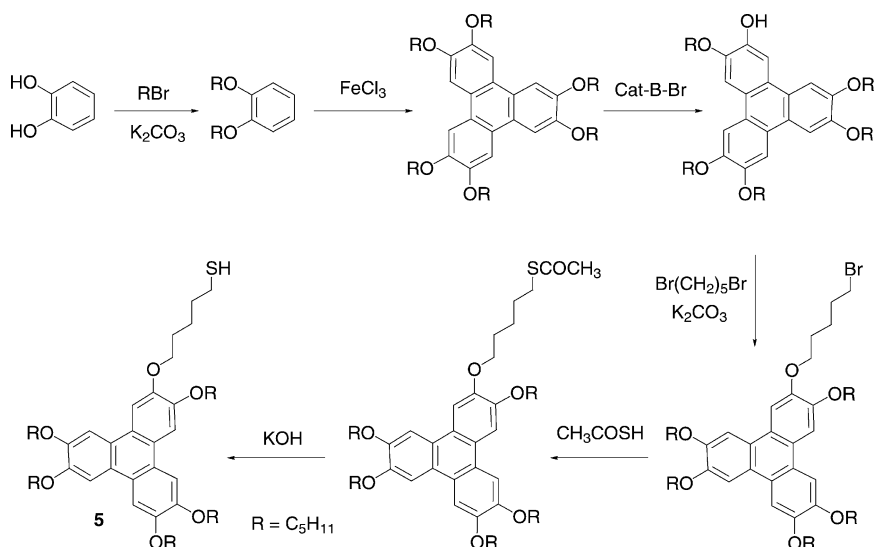


FIGURE 1 Chemical structures of (1) hexanethiolate-covered gold nanoparticle, (2) hexahexylthiotriphenylene, (3) hexahexyloxytriphenylene and (4) hexakis[4-(4-methylnonyl)phenylethynyl]benzene.

the complete removal of non-covalently bound organic material. Removal of the solvent afforded 60 mg of hexanethiol-capped gold nanoparticles. It has been determined that this procedure furnished 1.6 nm core diameter nanoparticles with an average composition of $\text{Au}_{140}[\text{S}(\text{CH}_2)_5\text{CH}_3]_{53}$ [7]. Three types of DLCs were synthesized to prepare GNP-DLC composites. These are hexahexylthiotriphenylene (HHTT) **2** displaying a highly ordered helical phase at lower temperature in addition to a hexagonal columnar mesophase [8], hexahexyloxytriphenylene (H6T) **3** having ordered hexagonal columnar phase [9] and hexakis[4-(4-methylnonyl)phenylethynyl]benzene **4** showing a discotic nematic phase at room temperature [10]. Binary mixtures

of GNPs with DLCs were prepared by mixing the two components in dichloromethane followed by removal of solvent and drying in vacuum. Five compositions (by weight) of GNPs:HHTT (**2a**, 1:4; **2b**, 1:3; **2c**, 1:2; **2d**, 1:1 and **2d**, 2:1), five compositions of GNPs:H6T (**3a**; 1:3; **3b**; 1:2; **3c**; 1:1, **3d**; 2:1, **3e** and 3:1) and 1:1 mixture GNPs-4 (**4a**) were prepared and analyzed by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Monothiol-functionalized triphenylene derivative **5** was prepared as shown in Scheme 1 using a combination of previously reported methods [9,11]. Mixed monolayer covered GNPs were prepared by mixing **1** (5 mg) and **5** (5 mg) in dichloromethane followed by removal of the solvent in vacuum. The purification was performed as described above for hexanethiol-protected GNPs. ^1H NMR analysis of the product indicates the presence of triphenylene and hexanethiol moieties in 1:1 ratio.

Measurement of conductivity was carried out using a standard DC voltage source (Aplab India), Picoammeter (Keithley 840) and a DMM (Keithley 2000). The samples were introduced into a glass capillary by heating to isotropic phase and then cooled to room temperature along with two gold coated copper wires at two ends which gets sealed during cooling. The resistance values are based on the measured current at different DC voltages in steps of 5 V up to 30 V. Current



SCHEME 1 Synthesis of thiol-functionalized triphenylene derivative.

measurements were also carried at different temperatures from $30 \pm 1^\circ\text{C}$ to $90 \pm 1^\circ\text{C}$ using the same measurement set-up.

RESULTS AND DISCUSSION

All the GNP-triphenylene DLC composites were found to be liquid crystalline in nature. They show classical textures of columnar mesophase upon cooling from the isotropic phase (Fig. 2). Thermal data for HHTT-GNP composites **2a–2e** have previously been reported [12]. Data obtained from the heating and cooling cycles of DSC for H6T-GNP composites **3a**, **3b**, **3c**, **3d** and **3e** are collected in Table 1. The DSC traces obtained on heating and cooling runs for **3c** (H6T-GNPs; 1:1 mixture) is shown in Figure 3.

In all the composites, the mesophase to the isotropic temperature broadened from about 2°C to about 8°C indicating a co-existence of the two phases. As may be seen from the DSC data plotted in graph 1, increasing the amount of GNPs decreases the mesophase isotropic temperature but the crystals to mesophase temperatures do not change significantly. This is logical as GNPs are expected to be inserted in between aromatic cores and, therefore, disruption of cores i.e., mesophase to isotropic temperature would be most affected. Phase segregation is also visible upon increasing the amount of GNPs. As the average composition of GNPs is $\text{Au}_{140}[\text{S}(\text{CH}_2)_5\text{CH}_3]_{53}$ [7], approximately one gold nanoparticle get incorporated in a column of about 40 triphenylene molecules in a 1:1 GNPs-H6T mixture. While HHTT and H6T composites show mesophases, a clear phase separation at about 75°C was observed in the case of discotic nematic-GNP (1:1) composite. In the nematic phase, there is only an orientational order

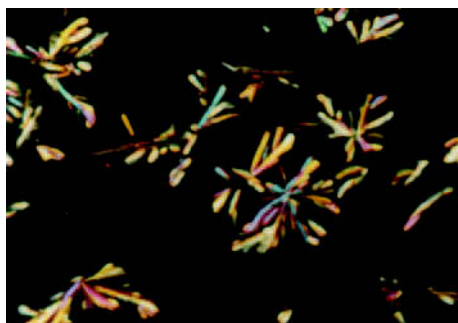
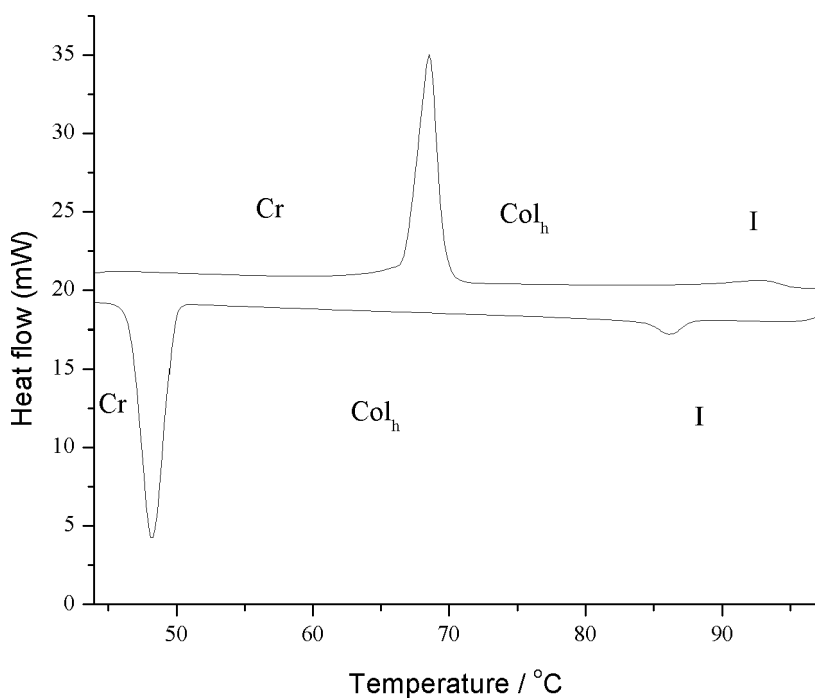


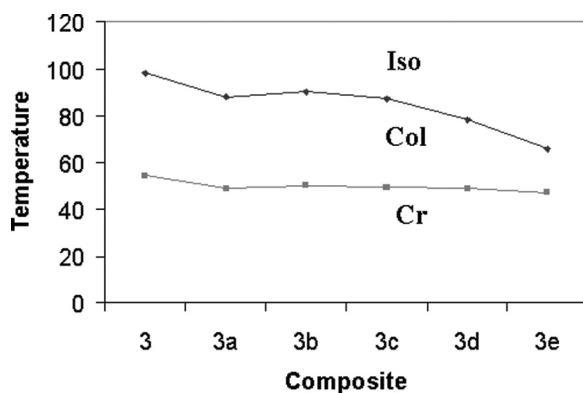
FIGURE 2 POM photograph of the columnar phase of **2c** at 83°C (crossed polarizers, magnification $\times 200$).

TABLE 1 DSC Rresults of GNP-H6T Composites. Cr = Crystalline, Col_h = Hexagonal Columnar Mesophase, I = Isotropic

Composite	Thermal transitions/°C	
	Heating scan	Cooling scan
3	Cr 68.2 Col _h 99.4 I	I 97.9 Col _h 54.5 Cr
3a	Cr 67.3 Col _h 92.5 I	I 88.2 Col _h 49.0 Cr
3b	Cr 67.4 Col _h 94.6 I	I 90.3 Col _h 49.9 Cr
3c	Cr 67.7 Col _h 92.1 I	I 87.0 Col _h 49.3 Cr
3d	Cr 66.9 Col _h 84.5 I	I 78.5 Col _h 49.0 Cr
3e	Cr 66.6 Col _h 74.8	II 65.8 Col _h 47.1 Cr

without any positional order of molecules and, therefore, the molecular interactions are not sufficient to hold the gold nanoparticles. On the other hand, in the columnar phases, the π - π interactions between aromatic cores are strong, which are likely to be responsible for retaining the nanoparticles in the column.

**FIGURE 3** DSC traces for composite **3c** on heating and cooling (scan rate 10°C min⁻¹).



GRAPH 1 Transition temperature of GNP-H6T composites.

CONDUCTIVITY MEASUREMENT

To check whether the inclusion of GNPs in the matrix of discotic liquid crystals increases the conductivity of these composites, we have measured the DC conductivity of the HHTT and HHTT:GNPs (1:1) composite by a four-point probe. Preliminary results indicate 250 times enhancement in the conductivity of HHTT upon doping with GNPs. We also found that upon increasing the temperature, a steady

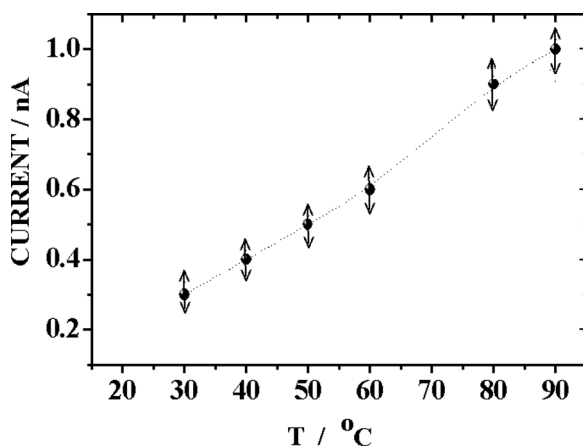


FIGURE 4 Plot of variation of current with temperature in GNP-HHTT (1:1) composite.

increase in the current was observed as shown in Figure 4. Detailed AC and DC conductivity experiments are in progress and will be published later.

CONCLUSION

Polarizing optical microscopy, differential scanning calorimetry and conductivity results indicate inclusion of thiolate-protected gold nanoparticles into a discotic liquid crystalline matrix. Increasing the amount of GNPs, increases the tendency of phase segregation and decreases the isotropic temperature. The conductivity of DLC-GNP composites is significantly higher compared with the pure discotic compound. Therefore, these inorganic-organic liquid crystal hybrid systems may be extremely important for many device applications such as photoconductors, light emitting diodes, photovoltaic solar cells, sensors, optical data storage, thin film transistors, etc.

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