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Inclusion of gold nanoparticles into a discotic liquid crystalline matrix†

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The thermophysical properties of mixtures of hexanethiolate-capped gold nanoparticles and three types of discotic liquid crystals, investigated using polarizing optical microscopy, differential scanning calorimetry and DC conductivity, indicate inclusion of gold nanoparticles into a matrix of triphenylene-based discotic liquid crystals.

The synthesis of monolayer-protected gold nanoparticles (GNPs) in organic solvents by Brust and co-workers[1] has opened up a whole new field in materials science. In the past decade about 1300 publications have appeared on the chemistry and physics of GNPs. The Brust method followed by several recent advances has allowed the facile synthesis of stable GNPs passivated with a variety of chemical functionalities.[2] These nanoparticles can be handled like simple organic materials. They can be dried of solvents and redissolved without core aggregation. Classical chemical reactions can be performed on functionalized GNPs.[2] Many of the physical properties of nano-sized metal particles are quite different from those of bulk materials. For instance, the conductivity of bulk gold is very high ($4.3 \times 10^7\ \Omega^{-1}\ \mathrm{m}^{-1}$) while GNPs of 1–2 nm are only semiconducting ($1.4 \times 10^{-3}\ \Omega^{-1}\ \mathrm{m}^{-1}$).[3] These organic-stabilized metal nanoparticles have potential applications in the field of catalysis, nonlinear optics, chemical and biological sensors, molecular recognition, nanotechnology *etc*.[2]

On the other hand, the past decade has also witnessed tremendous growth in the field of discotic liquid crystals (DLCs).[4] These supramolecular assemblies of disc-shaped molecules are of fundamental importance not only as models for the study of energy and charge migration in organized systems but also as functional materials for device applications such as one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors *etc*.[5] Owing to their remarkable electro-optical properties, a large number of DLCs have been prepared recently to study their various physical properties.[6] 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. Photo-induced charge carrier mobility (hole mobility) in the range of 10^{-3} $\mathrm{cm}^2\ \mathrm{v}^{-1}\ \mathrm{s}^{-1}$ to $0.71\ \mathrm{cm}^2\ \mathrm{v}^{-1}\ \mathrm{s}^{-1}$ has been reported in various columnar mesophases. Electroluminescence and photovoltaic devices based on DLCs have been prepared recently. The mechanism of charge transport and one-dimensional energy migration has also been studied extensively in these materials.[5]

Hybridization of these two fields may lead to novel materials with interesting properties that are 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. In this communication, we report the mesomorphic properties of GNP–DLC composites.

Hexanethiolate-stabilized gold clusters **1** (Fig. 1) were prepared by following the reported method exactly.[7] It has been determined that this procedure furnished 1.6 nm core diameter nanoparticles with an average composition of $\mathrm{Au_{140}[S(CH_2)_5CH_3]_{53}}$.[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] hexapentyloxytriphenylene (H5T) **3** having an ordered hexagonal columnar phase[9] and hexakis(4-nonylphenylethynyl)benzene (H9B) **4** showing a discotic nematic phase.[10] Binary mixtures of GNPs with DLCs were prepared by mixing the two components in dichloromethane followed by removal of solvent and drying under vacuum. Four compositions (by weight) of GNPs–HHTT (**2a**, 1 : 4; **2b**, 1 : 3; **2c**, 1 : 2 and **2d**, 1 : 1) and 1 : 1 mixtures of GNPs–H5T (**3a**) and GNPs–H9B (**4a**) were prepared and analyzed by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

All the GNP–triphenylene DLC composites **2a, 2b, 2c, 2d** and **3a** were found to be liquid crystalline in nature. They show classical textures of columnar mesophases upon cooling from the isotropic phase (Fig. 2). Data obtained from the heating and cooling cycles of DSC are collected in Table 1. The DSC traces obtained on heating and cooling runs for **2d** (HHTT–GNPs; 1 : 1 mixture) are shown in Fig. 3. DSC traces of **2**, **2a**, **2b**, **2c**, **3** and **3a** are given in the

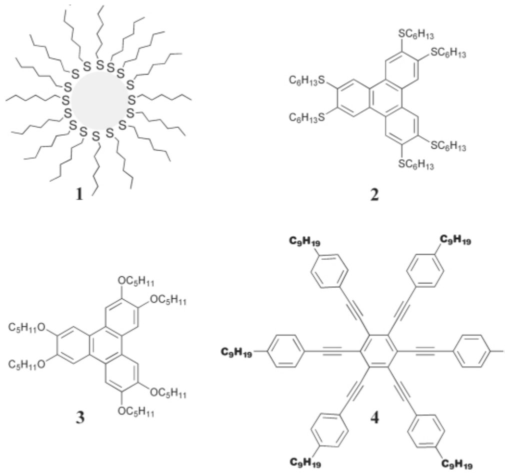

Fig. 1 Chemical structures of hexanethiolate-covered gold nanoparticle (**1**), hexahexylthiotriphenylene (**2**), hexapentyloxytriphenylene (**3**) and hexakis(4-nonylphenylethynyl)benzene (**4**).

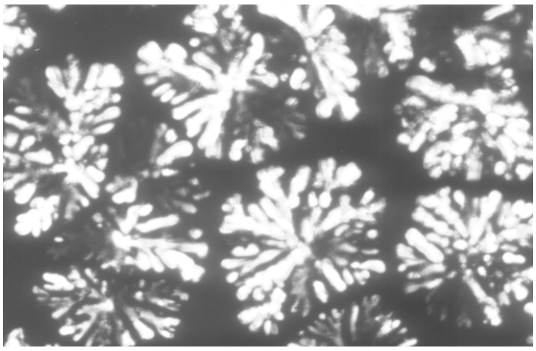

Fig. 2 POM photograph of the columnar phase of **2b** at 85 °C (crossed polarizers, magnification × 200).

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† Electronic supplementary information (ESI) available: DSC traces and POM pictures. See http://www.rsc.org/suppdata/cc/b4/b403794d/

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Electronic Supplementary Information.† POM pictures of **2a**, **2b** and **3a** at 66.7 °C, 80 °C and 104 °C respectively, have also been provided in the ESI.

As may be seen from the data, increasing the amount of GNPs decreases the mesophase isotropic temperature but the crystals to mesophase or mesophase to mesophase (helical phase to columnar phase) temperatures do not change significantly. This is logical as GNPs are expected to be inserted in between aromatic cores and, therefore, disruption of the cores *i.e.* mesophase to isotropic temperature would be most affected. As the average composition of GNPs is $Au_{140}[S(CH_2)_5CH_3]_{53}$,[7] approximately one gold nanoparticle gets incorporated in a column of about 36 triphenylene molecules in a 1 : 1 GNP–HHTT mixture. It is well known that thiols, disulfides and thioethers interact strongly with gold covered substrates and we have previously shown the self-assembly of HHTT on gold.[11] However, such physical adsorption of HHTT can be ruled out as the gold nanoparticles are covered with a hexanethiolate monolayer and, therefore, HHTT molecules can not come into the proximity of the gold nanoparticle surface. Furthermore, the observation of a columnar phase in the GNPs–H5T composite also indicates that it is not the physical adsorption of thioethers (present in HHTT), but π–π interactions of aromatic cores, that are primarily responsible for holding the nanoparticles in the column. It is also evident from the fact that the gold nanoparticle–discotic nematic composite **4a** shows a clear phase separation at about 83 °C. Since in the nematic phase, there is only an orientational order without any positional order of molecules, the intermolecular interactions are not sufficient to retain the gold nanoparticles.

The conductivity of the HHTT and HHTT : GNP (1 : 1) composite **2d** was measured by a four-point probe. Preliminary results indicate 250 times enhancement in the DC conductivity of HHTT upon doping with GNPs. Detailed AC and DC conductivity experiments are in progress and will be published later.

Table 1 DSC results of GNP–DLC composites. Cr = crystal, H = helical phase, Col_h = hexagonal columnar mesophase, I = isotropic

	Thermal transitions/°C	
Composite	Heating scan	Cooling scan
2	Cr 67 H 74.9 Col_h 93.4 I	I 91.1 Col_h 66.8 H
2a	Cr 66.4 H 74.1 Col_h 90.1 I	I 86 Col_h 65.7 H
2b	Cr 67 H 74.7 Col_h 90.3 I	I 85.8 Col_h 65.8 H
2c	Cr 66.9 H 73.9 Col_h 88.3 I	I 83.6 Col_h 65.7 H
2d	Cr 67.7 H 74.4 Col_h 86.6 I	I 81.6 Col_h 65.5 H
3	Cr 65 Col_h 122.6 I	I 121.1 Col_h 46.3 Cr
3a	Cr 64.4 Col_h 109 I	I 106 Col_h 52.2 Cr

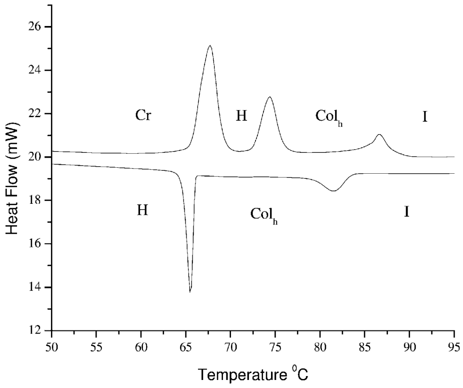

Fig. 3 DSC traces for composite **2d** on heating and cooling (scan rate 10 °C min^{-1}).

In conclusion, POM, DSC and conductivity results indicate intercalation of GNPs into the matrix of discotic liquid crystals. While a minor shift in the transition temperatures was observed, the nature of the mesophases is not altered in these composites. However, more experiments are required to understand the supramolecular nature of these DLC–GNP composites. 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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