

The Design and Investigation of Room Temperature Thermotropic Nematic Gold Nanoparticles

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The controlled spatial assembly of metallic nanoparticles of defined size and shape in organic matrixes has recently received great attention, as such materials promise synergistic property combinations in the self-assembled state.^{1–4} However, to achieve such unique properties, nanoparticles of narrow or ideally uniform size distribution have to be functionalized with suitable organic groups, and these materials have to be organized and oriented. In the area of LC research, the recent observation that the incorporation of “spherical” nanoparticles into nematic liquid crystals (nematic LCs) can enhance the dielectric response and conversely the switching speed significantly is of great technological importance and adds impetus to research into LC nanoparticles.^{5,6} This is particularly relevant since, to date, no nanoparticles have been reported which have been functionalized so that nematic phase behavior is obtained. A key challenge for such systems is associated with the control of the LC phase structure and the stability of the systems over a suitable (ideally room temperature and above) temperature interval.

Here we report on the investigation of the first LC gold nanoparticle system which exhibits a thermotropic nematic phase in the bulk. The system was designed to show LC behavior at room temperature.

The main challenge in the design of the material was to reconcile the shape of the nanoparticles (approximated as spherical) with the nematic phase structure, characterized by only orientational long-range ordering in one direction and the absence of positional order. To achieve nematic phase behavior, mesogen **1**, shown in Figure 1 (the hydrogen linked to the thiol group has been omitted in the figure), was selected. The rod-like system consists of three aromatic rings flanked by flexible alkyl chains of eight and eleven methylene groups at the termini of the rod-like mesogen. The compound can be connected to the gold particle via a thiol group at the terminus of a laterally attached spacer consisting of eleven methylene groups. This class of materials has been found to promote nematic phase behavior in polymers, organic–inorganic hybrids, and dendrimers.^{7,8}

It was decided to synthesize nanoparticles with diameters in the region of 1.6–2 nm.⁹ For particles of this size, the polydispersity can be controlled well, and size variations are much smaller than the length of a fully extend mesogen (~4 nm), and it was judged that this approach would rationalize the evaluation of structure–property relationships. Furthermore, such particles can still be approximated as spheres, at least for initial studies, as none of the crystal faces of the nanoparticles is large when compared to the overall size of the particles.^{10,11} In reality, the materials are likely to consist of truncated octahedral or decahedral nanocrystals.¹² Initial studies of nanoparticles covered only with **1** showed the loss of mesomorphic behavior, and only a glass transition was observed. At high levels of surface coverage, this was attributed to the loss

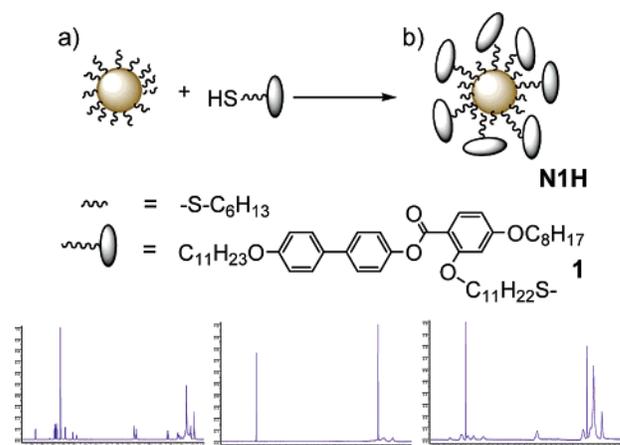


Figure 1. Top: Schematic representations; (a) (left) nanoparticles and (b) (right) exchange reaction yielding **N1H**. Middle: Chemical structure of the groups covering the particle surface (hexylthiol and mesogen). Bottom: NMR spectrum of mesogen **1** (left), NMR spectrum of hexylthiol-functionalized nanoparticle; LC nanoparticle **N1H** (right).

of orientational mobility of the mesomorphic groups attached to the core, due to steric crowding. For partial coverage of the surfaces of particles with mesogens, it was found that the resulting materials were not thermally stable at elevated temperatures, either due to delamination of the thiol-containing mesogens (cleavage of Au–S bonds, detectable by ¹H NMR, the signal for the terminal methylene group reappears) or possibly also due to a reorganization of the surfaces.^{10,11} Nematic nanoparticles were finally obtained by the attachment of hydrocarbon chains as well as mesogens in a two-step synthetic process, as shown schematically in Figure 1.^{13,14} First, gold particles, which are covered with a hydrocarbon monolayer (hexylthiol chains), were synthesized, and in a second step, the surface was functionalized further. The hexylthiol-covered gold nanoparticles were reacted with mesogen **1** in dichloromethane at ambient temperature for 3 days to form the monolayer-protected LC gold nanoparticles **N1H** in an exchange reaction.^{14,15}

The ¹H NMR spectra of the investigated nanoparticles and the comparison with the spectrum of **1** (Figure 1) indicate that the thiol groups of both hydrocarbons and mesogens are chemically attached to the surface of the gold particles and are not present as free thiols. The spectra of the nanoparticles are broadened when compared to those of the free thiols, and the peaks (¹H) at δ 1.08 ppm (–SH) and 2.15 ppm (–CH₂–SH) present in the free thiols have disappeared, typical for such systems.^{9,12a} The amount of **1** bound to the surfaces relative to the number of hexylthiol groups was determined from the ¹H NMR spectra of **N1H**.¹³ The ratio of hydrocarbons to mesogens was found to be 1:1. Transmission electron microscopy (TEM) investigations confirm that this sequential synthesis affords nanoparticles of low polydispersity.^{12,16} An example of a TEM picture is shown in Figure 2 (left).

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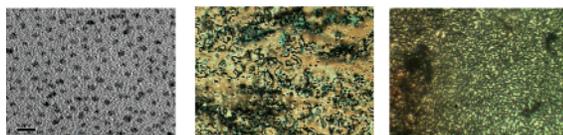


Figure 2. TEM picture of the **N1H** (left) on a graphite surface, scale bar = 5 nm; OPM pictures of **1** (middle) and **N1H** (right) (magnification for OPM pictures $\times 100$).

Table 1. Transition Temperature ($^{\circ}\text{C}$) as Determined by DSC (second heating, $2^{\circ}\text{C min}^{-1}$)^a

Compound		Transition temperature/ $^{\circ}\text{C}$ (Enthalpy Jg^{-1})			
1	Cr	81.3	(N,	61.3 (1.72))	Iso
N1H	Tg	-3	N,	43.8 (0.60)	Iso

^a Cr = crystalline, Tg = glass transition, N = nematic, Iso = isotropic.

The data gained from TEM experiments allow an estimation of the average particle size of 1.6 ± 0.4 nm. The combination of elemental analysis, $^1\text{H NMR}$, and TEM data allowed an evaluation of the composition of the hydrocarbon and mesogen monolayer.¹⁷ The number of gold atoms per particle can be estimated to be 140 gold atoms/particle, and the number of surface-attached chains can be approximated to 53 ± 5 for **N1H**.

In other words, the polymer analogous-type of exchange reaction resulted in a material where, on average, approximately 25–30 mesogens (ratio of 1:1 hexylthiol groups/**1**) have been attached to the gold nanoparticles. The mesogen-functionalized **N1H** system was found to exhibit enantiotropic nematic phase behavior. The stability of the system in the nematic phase was verified with NMR studies (spectra were collected after annealing bulk samples in the nematic phase), and no sign of degradation (e.g., the formation of free thiols) was observed. The thermal transitions determined by differential scanning calorimetry (DSC) for **1** and **N1H** are collected in Table 1.¹⁵ A sharp peak associated with the isotropic to nematic transition can be detected, and at low temperature (-3°C), a glass transition occurs. The value for the transition enthalpy (ΔH) of 0.60 Jg^{-1} for the nanoparticle **N1H** system is broadly similar to those observed for organic/inorganic hybrids and dendrimers containing structurally related mesogenic groups.⁸ The enthalpy values are relatively low when compared to those of many other liquid crystal systems, suggesting the presence of a low ordered system, a result to be expected considering the geometry and structure of **N1H**. Figure 2 shows the optical polarizing micrographs (OPM) of **1** and **N1H**, and the thermal transitions are listed in Table 1. After annealing, the gold particles form the typical nematic marbled and *Schlieren* textures (an example is shown in Figure 2 (right)), which are much less well defined than those observed for the mesogen **1** (Figure 2, middle), a feature found for many LC polymers.¹⁸ It is noted that the **N1H** system shows complete miscibility with the mesogen **1** and its olefinic mesogenic precursor.¹⁵

In summary, we have prepared novel nematic gold nanoparticles, where the spherical particles are covered with a monolayer of

calamitic mesogens and short hydrocarbon chains. The materials are chemically stable and exhibit nematic phase behavior at room temperature.

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Supporting Information Available: Experimental procedures for the synthesis of the materials, and the DSC characterizations are described. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) See Supporting Information.
- (16) (a) The number of gold atoms/particle was calculated using the following formula from refs 13 and 14: $N_{Au} = 4\pi R^3/3v_g = 4\pi D^3/8 \times 51$, where R is the radius of nanoparticle (\AA) gained from TEM; D is the diameter of the nanoparticle (\AA); v_g refers to volume of a gold atom ($v_g = 17 \text{\AA}^3$). (b) It should be noted that, due to the strong absorption of the nanoparticles in the visible, the films have to be very thin to record OPMs of typical defect textures.
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