The design and investigation of room temperature thermotropic nematic gold nanoparticles

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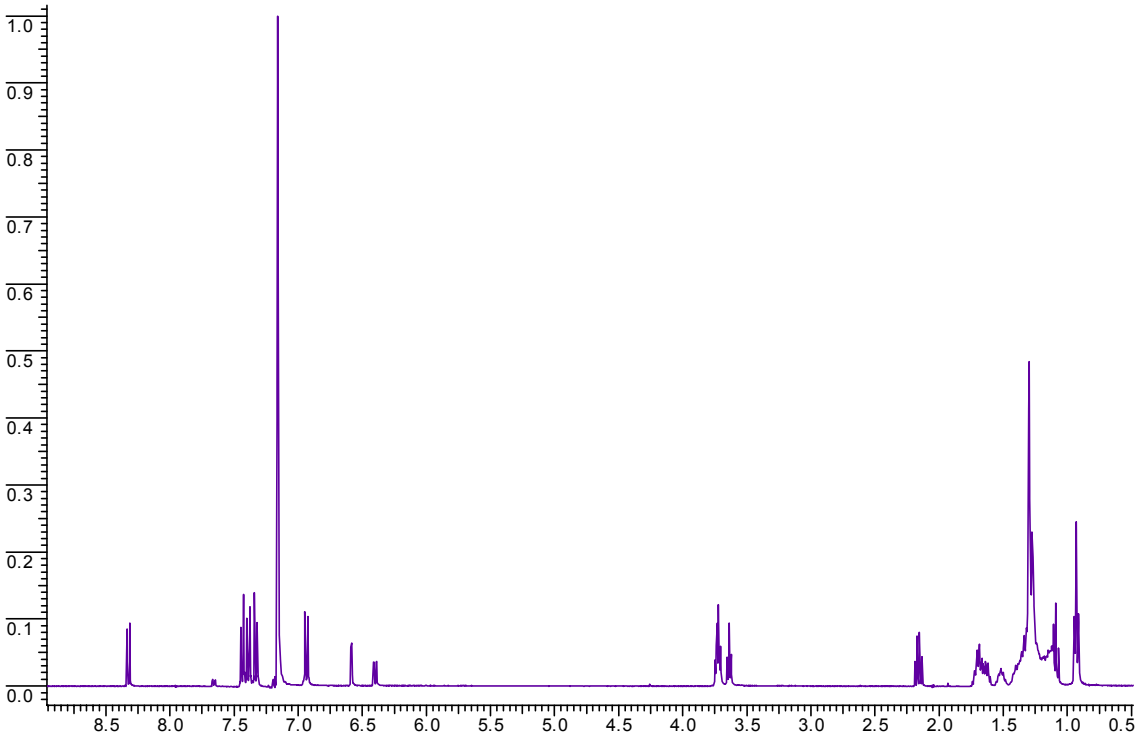
Supporting information

Instrumentation

Nuclear magnetic resonance (NMR) spectra were taken on a Jeol JNM-ECP 400 MHz FT-NMR spectrometer. Chemical shifts are reported in ppm relative to TMS. The thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC) 822^e in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software *Studio Capture*, supplied by Studio86Designs was used for image capturing. Transmission electron micrographs were recorded with a JEOL JEM 3010 Transmission Electron Microscope (point resolution 0.17 nm).equipped with a GATAN GIF 200 electron imaging filter.

NMR Spectra (solvent $CDCl_3$: a) **1**; b), hexylthiol substituted nanoparticle system; c) **N1H**.

a)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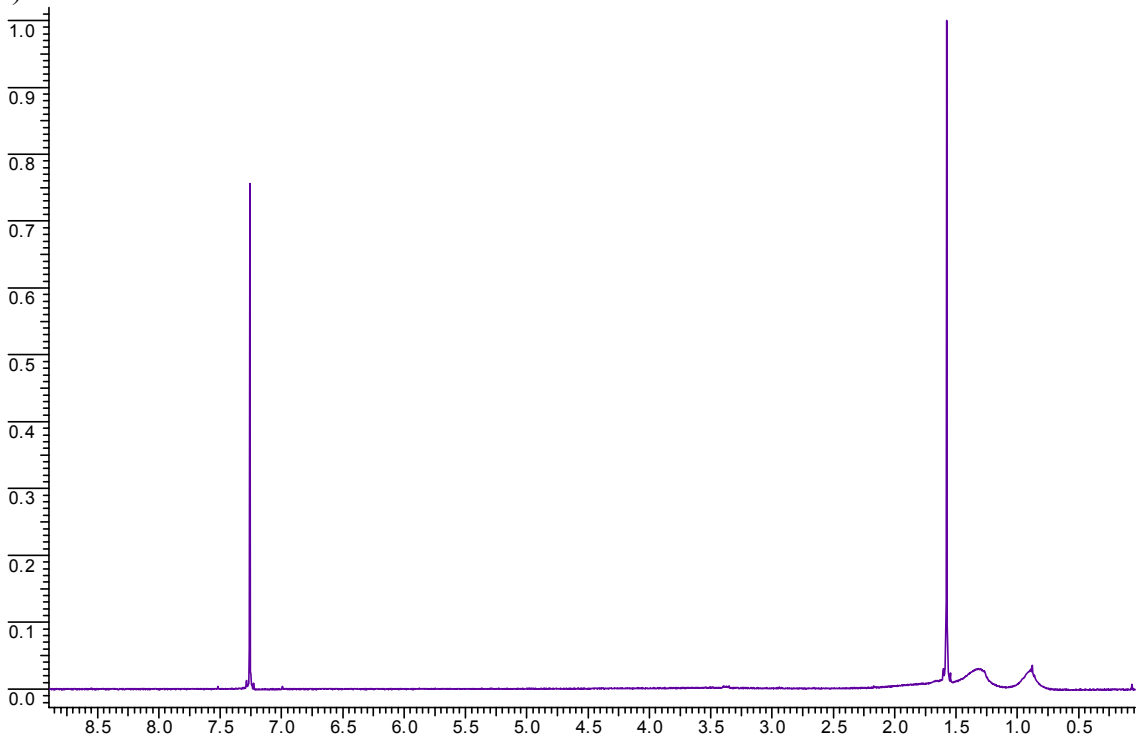
b)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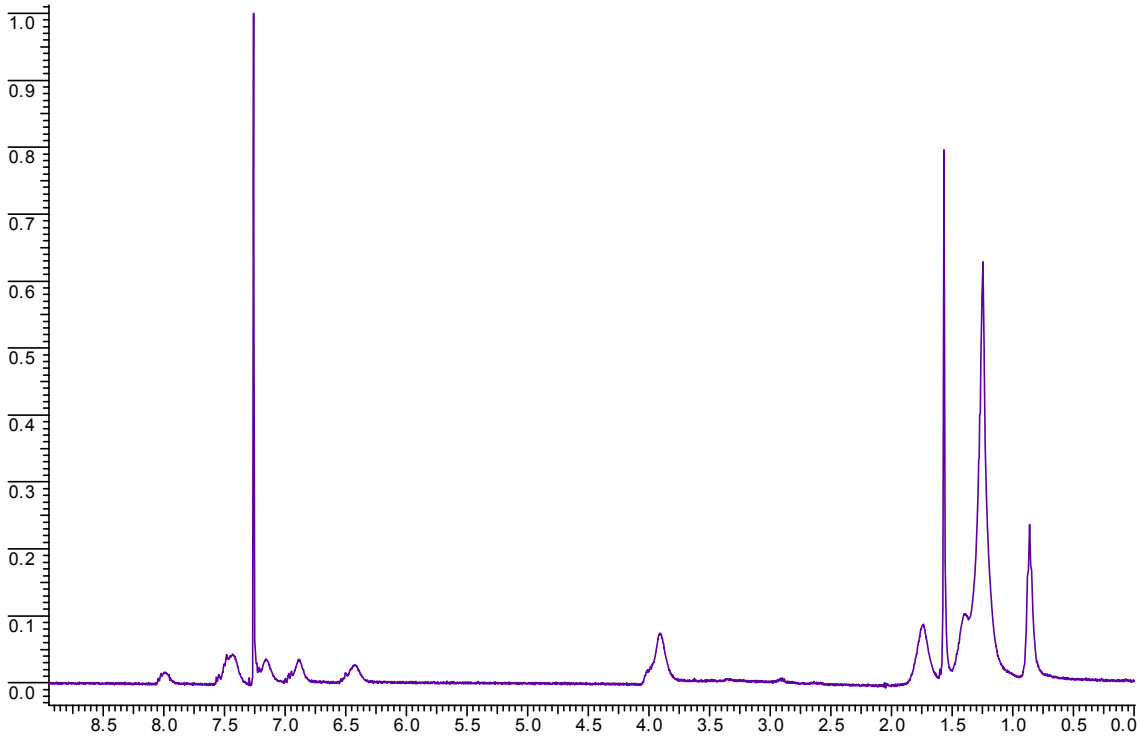
c)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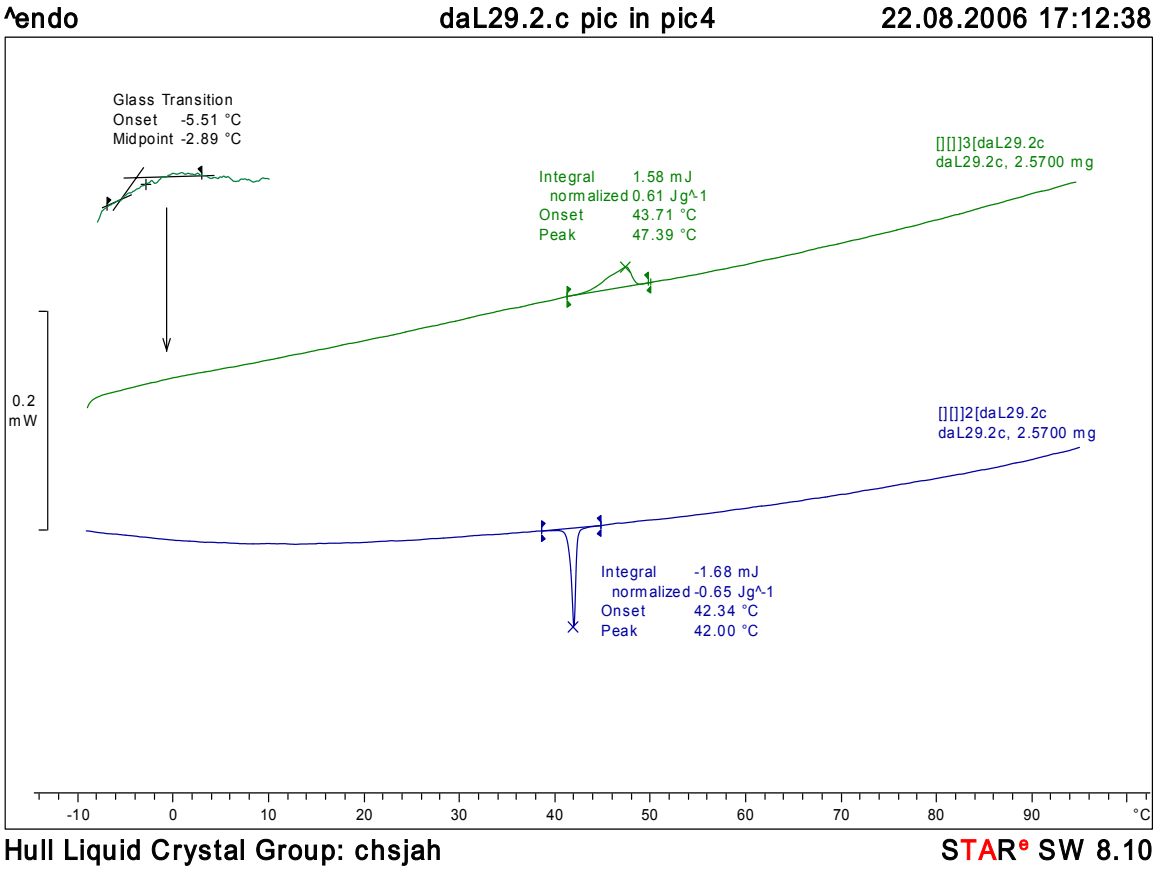
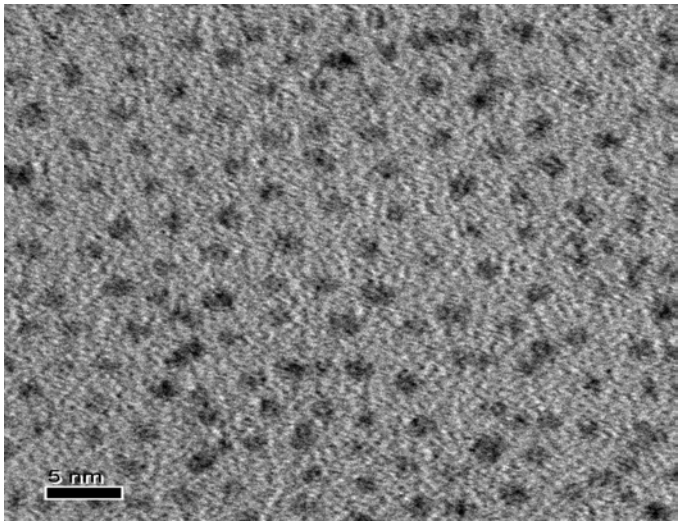
DSC trace of **N1H**. The glass transition has a very low ΔCp value, and was therefore not analyzed further.



TEM picture of **N1H** on a graphite surface. Scale bar = 5 nm



Calculation of the of the number of organic groups covering the surface of the napoarticles

The number of gold atoms/particle was calculated using the following formula [1, 2]:

$$N_{Au} = \frac{4 * \pi * R^3}{3 * \nu_g} = \frac{4 * \pi * D^3}{8 * 51}$$

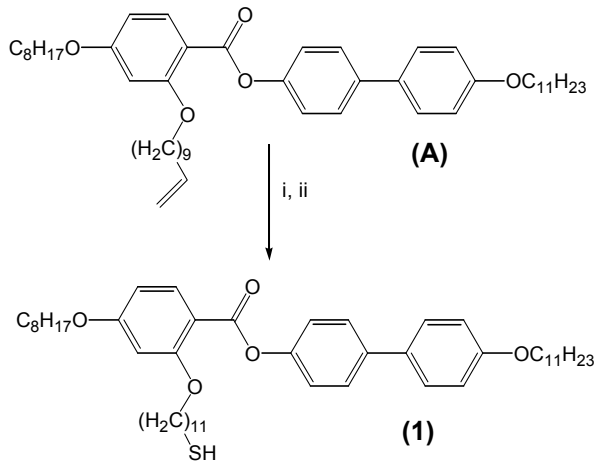
where: R – radius of nanoparticle (Å); D – diameter of nanoparticule (Å); ν_g – volume of gold atom ($\nu_g = 17$ Å^3).

The diameter of nanoparticles was determined by transmission electron microscopy (TEM). The dimension of nanoparticles was determined to be 1.6 ± 0.4 nm. Each particle contains about 140 gold atoms/ particle.

The ^{1}H-NMR spectra were used to prove the purity of nanoparticles and to calculate the ratio of alkaneanthiol to mesogens **1** attached to a particle.

Synthesis of 1

The compound 4'-(undecyloxy)biphenyl-4-yl 2-(11-mercaptoundecyloxy)-4-(octyloxy) benzoate **(1)** was obtained in two steps. The first step is free-radical addition reaction induced by AIBN as initiator [3] to the starting material **A** [4] and the second step is a mild deprotection reaction, which was carried out using TFA at room temperature. The thiol was isolated by column chromatography (SiO_2, CH_2Cl_2/hexane = 6/4, Rf = 0.43). Recrystallization from hexane yielded a white solid product.



Scheme 1. *Reagents and conditions*: i), Ph_3SiSH (1.4 eq), AIBN, benzene, reflux 38h; ii), TFA (5 eq), room temperature, 30 min.

(1) Yield: 34%; elemental analysis calc. for $C_{49}H_{74}O_5S$, C, 75.92; H, 9.62; S, 4.14. Found: C, 75.80; H, 9.50; S, 4.19 %;
^{1}H-NMR (400 MHz in C_6D_6) δ[ppm]: 0.92(t, 6H, -CH_3), 1.08(t, 1H, -SH), 1.10-1.55(m, 42H, -CH_2-), 1.66(m, 6H, -CH_2-), 2.15(dt, 2H, -C**H_2**-SH), 3.62(t, 2H, -O-CH_2-), 3.71(m, 4H, -O-CH_2-), 6.39(d, 1H, $H_{ar.}$), 6.57(dd, 1H, $H_{ar.}$), 6.93(m, 2H, $H_{ar.}$), 7.32(m, 2H, $H_{ar.}$), 7.38(m, 2H, $H_{ar.}$), 7.42(m, 2H, $H_{ar.}$), 8.31(d, 1H, $H_{ar.}$);

^{1}H-NMR of **NH1:** (400 MHz in $CDCl_3$) δ[ppm]: 0.86(-CH_3), 1.24(-CH_2-), 1.74(-CH_2-), 3.88(-O-CH_2-), 6.41(H_{ar}), 6.86(H_{ar}), 7.13(H_{ar}), 7.43(H_{ar}), 8.02(H_{ar}).

The results on nanoparticles partially covered with LC groups, not showing liquid crystalline behavior in the bulk have been reported as a poster presentation in: L.Cseh, G.H Mehl, Poster COL-P056, Book of Abstracts, 20th Int. Liquid Crystal Conf, 04-09. 07. 2004, Ljubljana, Slovenja.

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