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) 822e 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 CDCl₃: a) I; b), hexylthiol substituted nanoparticle system; c) N1H.
DSC trace of N1H. The glass transition has a very low $\Delta C_p$ value, and was therefore not analyzed further.

TEM picture of N1H on a graphite surface. Scale bar = 5 nm
Calculation of the number of organic groups covering the surface of the nanoparticles

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

\[
N_{Au} = \frac{4 \pi R^3}{3 \nu_g} \approx \frac{4 \pi D^3}{8 \nu_g}
\]

where: \(R\) – radius of nanoparticle (Å); \(D\) – diameter of nanoparticle (Å); \(\nu_g\) – volume of gold atom (\(\nu_g = 17 \text{ Å}^3\)).

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 alkaneanethiol to mesogens \(1\) attached to a particle.

Synthesis of \(1\)

The compound 4'-(undecyloxy)biphenyl-4-yl 2-(11-mercaptopundecyloxy)-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\(_2\)Cl\(_2\)/hexane = 6/4, Rf = 0.43). Recrystallization from hexane yielded a white solid product.
Scheme 1. Reagents and conditions: i), Ph$_3$SiSH (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$_5$S, 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$_6$D$_6$) 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, -CH$_2$-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 NH$_1$: (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, 20$^{th}$ Int. Liquid Crystal Conf, 04-09. 07. 2004, Ljubljana, Slovenija.