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Structure property relationships in 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.

Experimental section

Monolayer-protected clusters (N-A6 and N-A12) covered with alkanethiolate monolayers were prepared via a modification of the "Brust-Schiffrin" method [1], a 2:1, or respectively a 1.66:1 molar ratio of thiol and gold (1mmol) was combined and allowed to react in toluene, reductant ($NaBH_4$) was added at 0°C for A6 and room temperature for A12, and the dark products solution were stirred for 3 h at room temperature. The organic phase was separated from aqueous phase, its volume was reduced to 10 ml, and 400 ml of ethanol was added. The mixture was kept at -18°C for 14h. The resulting black precipitate was collected on a frit and thoroughly washed with ethanol.

Place-exchange reactions of the alkanethiol groups with thiol **1** groups were effected by stirring a dichloromethane solution containing a 1.5-fold molar excess (relative to these alkanethiol on the A6 and A12) of the mesogenic ligand. After three days the solvent was removed under reduced pressure. The mixed monolayer N-A6, N-A12 was purified by sonication in ethanol and acetone. The ensuing black solids were dried under vacuum. The materials are air-stable and soluble in chloroform, toluene, dichloromethane, hexane, and other nonpolar solvents.

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]:

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

where: R – radius of nanoparticle (Å); D – diameter of nanoparticule (Å); ν_g – volume of gold atom (ν_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.

[1] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, Chem. Commun, 1994, 801-802.

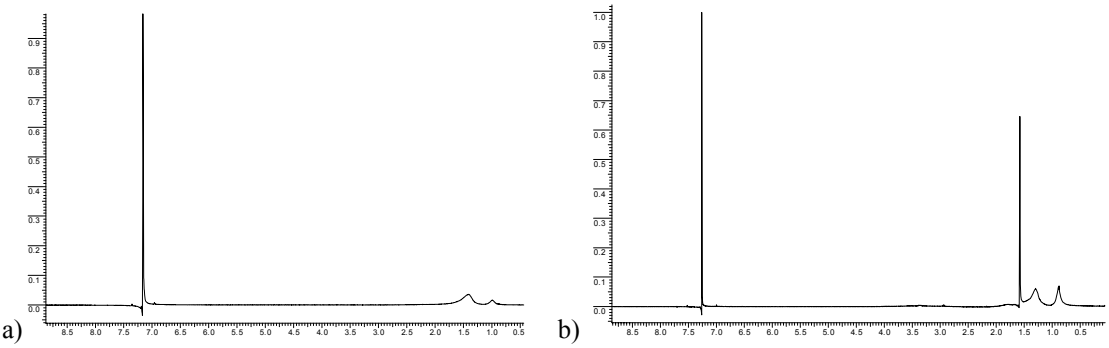

Figure ^{1}H-NMR spectra in $CDCl_3$ of **A12** (a) and **A6** (b) The large peak at 1.53 ppm is due to H_2O.