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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** GI-SAXS studies of molecular ordering in alkane chains and DNA lattices	**Experiment number**: 28 01 789
Beamline: BM28	**Date of experiment**: from: 16 May 2007 to: 22 May 2007	**Date of report**: 30 Sept 2008
Shifts: 17	**Local contact(s)**: Dr. Danny MANNIX	*Received at ESRF:*

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Report:

The original aim of this experiment was to investigate ordering in monolayers of alkanes on HOPG surfaces and DNA lattices on mica surfaces. Alkanes $C_{60}H_{122}$ and $C_{122}H_{246}$ were prepared by S Maganov, (Veeco) and DNA tiled lattices by HaoYan's group, Arizona. Grazing incidence SAXS and WAXS were performed for the alkanes, and SAXS was performed on the DNA lattices in both grazing incidence and transmission geometry. In both cases, no diffracted signal could be observed from the monolayers. It is unclear whether this was caused by rapid beam damage.

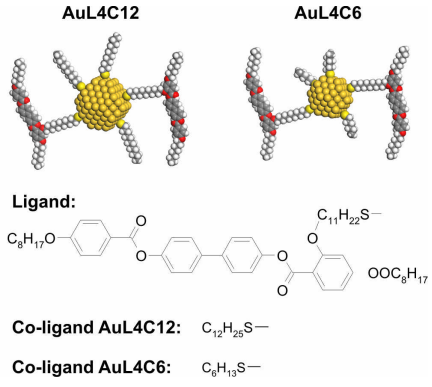

Figure 1. Schematic structure of the gold nanoparticles coated with mesogen and dodecylthiol (compound **AuL4C12)** or hexylthiol chains (compound **AuL4C6)**.

The remainder of the beamtime was used to study two samples as a feasability study for nanoscale ordering of metallic nanoclusters. It has been predicted theoretically [1] that metamaterial devices with interesting optical properties such as band pass filtering could be generated from well-ordered 3D arrays of nanoparticles much smaller than the wavelength of light, spaced at a controlled distance from each other. Ordered clusters of such lattices, also producing resonances in permeability, could then lead to negative refractive index in a wide spectral range including the visible [2]. Metal nanoparticles derivatized with alkane thiols, acids or amines could only be made to form bulk lattices with long-range order if they were highly monodisperse [3]. We investigate small gold nanoparticles (ca. 2 nm in diameter) covered by a mixture of a rod-like mesogen and thioalkanes (of two different lengths) (Fig 1) in an attempt to exploit the liquid crystalline interactions [4].

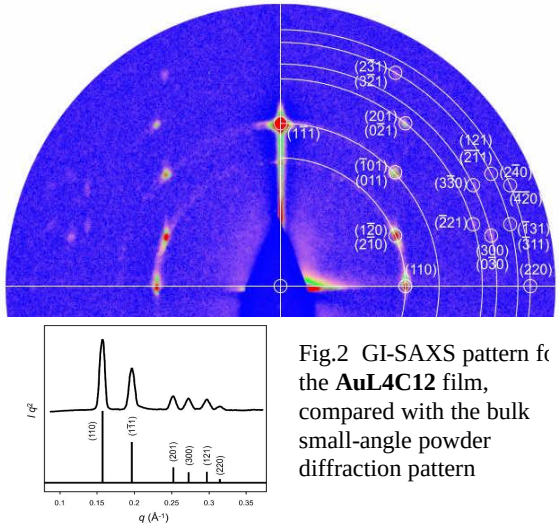

Fig.2 GI-SAXS pattern fo the **AuL4C12** film, compared with the bulk small-angle powder diffraction pattern

A previously-measured powder SAXS pattern of **AuL4C12** is shown in Fig 2, displaying six diffraction peaks. The GI-SAXS measurement show far more structural information. As shown in Figure 2(b), the GISAXS pattern can be indexed well on a rhombohedral lattice with space group $R\bar{3}m$. The orientation is of the fibre type, i.e. with the domains cylindrically averaged around the $[1\bar{1}1]$ axis which is perpendicular to the substrate surface – see also Figure 2c. The unit cell parameters are a = 80.0 Å, c = 35.4 Å. With the diffraction peaks indexed and space group determined, we proceeded to reconstruct the electron density map using the measured diffraction intensities. Since the structure has an inversion centre, one can write $E(x,y,z) = \sum_{h,k,l} \sqrt{I(h,k,l)} \cos[2p(hx+ky+lz) + f_{h,k,l}]$ where the phase angle $f_{h,k,l}$ for each diffraction order is either 0 or π. However, as the phase angle can not be directly determined from the X-ray data, the choice of phase combination was made on the basis of the physical merits of the electron density map, with the help of existing knowledge of the system. The right phase combination gives well defined low and high density regions, due to the high contrast in electron density between gold nanoparticles and their surroundings. As only a few peaks were observed for each mesophase all possible phase combinations were examined, and the best solution was decided on the basis of the electron density maps and histograms obtained.

The resulting 3-d map in Figure 3(a) shows that the gold nanoparticles arrange in columns along the [001] direction. The columns pack on a simple triangular lattice, clear when viewed along the [001] direction.

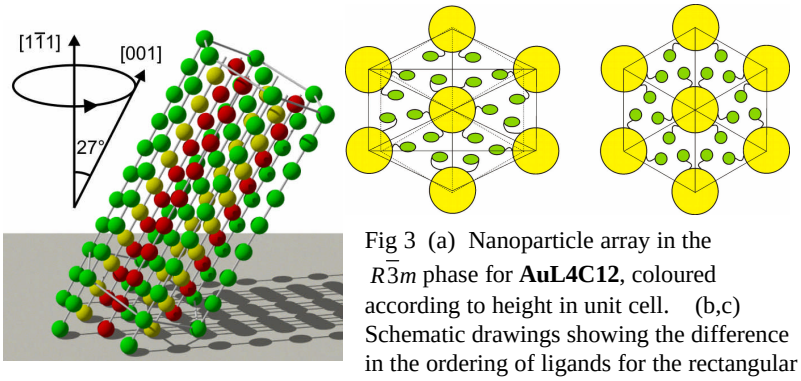

Fig 3 (a) Nanoparticle array in the $R\bar{3}m$ phase for **AuL4C12**, coloured according to height in unit cell. (b,c) Schematic drawings showing the difference in the ordering of ligands for the rectangular (30°C) and hexagonal (90°C) phases.

For **AuL4C6**, the nanoparticles with the shorter hexylthiol co-ligand chains, a plane group *c*2*mm* with *a* = 74.4Å, b=40.8Å was obtained for 30-80°C. At 90 °C and 100 °C the lattice is 2D hexagonal, *p*6*mm*, with *a* = 41.0 Å. 2D electron density maps of both the rectangular and hexagonal phases were reconstructed. The resulting structures are shown schematically in Figures 3(b,c). The large circles are the projections of the nanoparticle columns, surrounded by the nematogenic rod-like ligands viewed along their long axis (small circles or ellipses). The arrangements of the columns in the two phases are similar: the centred rectangular phase transforms to the hexagonal by shrinkage in the *a* direction until the *a/b* ratio drops to $\sqrt{3}$. The reconstructed maps indicate that the nanoparticles in **AuL4C6** also form columns as in **AuL4C12**. However, only two dimensional long range ordering of column axes exists in **AuL4C6**.

The mesophase structure of both **AuL4C12** and **AuL4C6** can be described as consisting of columns of nanoparticles surrounded by a sheath of axially aligned mesogens. While with dodecylthiol chains in **AuL4C12** the interparticle gap along the column is kept at 16.5 Å (Figure 4a), by changing to hexylthiol in **AuL4C6** the gap is reduced to a mere 4.8 Å in the *p*6*mm* phase (Figure 4b). This work demonstrates that highly ordered superlattices of metal nanoparticles other than those expected from mere packing of spheres can be created by coating the particles with a laterally attached nematogenic ligand. The results give the first rules on which to base future designs of more complex lattices with a view to build self-assembled metamaterials. Work on new gold nanoparticle superlattices is in progress. We have a paper in draft form to be submitted shortly.

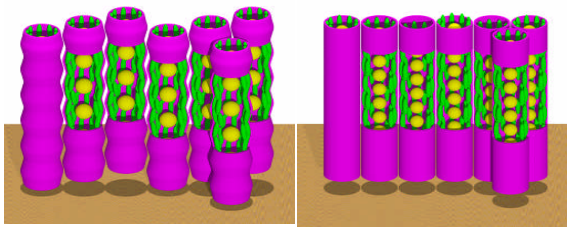

Figure 4 Schematic models of the (a) rhombohedral phase in **AuL4C12** and (b) the hexagonal columnar phase in **AuL4C6**; yellow: gold nanoparticles, green: mesogens.

References

[1] Rockstuhl, C. & Scharf, T. A metamaterial based on coupled metallic nanoparticles and its band-gap property. *J. Microscopy* **229**, 281-286 (2008).

[2] Rockstuhl, C., Lederer, F., Etrich, C., Pertsch, T. & Scharf, T. Design of an Artificial Three-Dimensional Composite Metamaterial with Magnetic Resonances in the Visible Range of the Electromagnetic Spectrum. *Phys. Rev. Lett.* **99**, 017401 (2007).

[3] Whetten, R.L. et al. Nanocrystal gold molecules. *Adv. Mater.* **8**, 428-433 (1996).

[4] Cseh, L. & Mehl, G.H. Structure-property relationships in nematic gold nanoparticles. *J. Mater. Chem.* **17**, 311-315 (2007).