

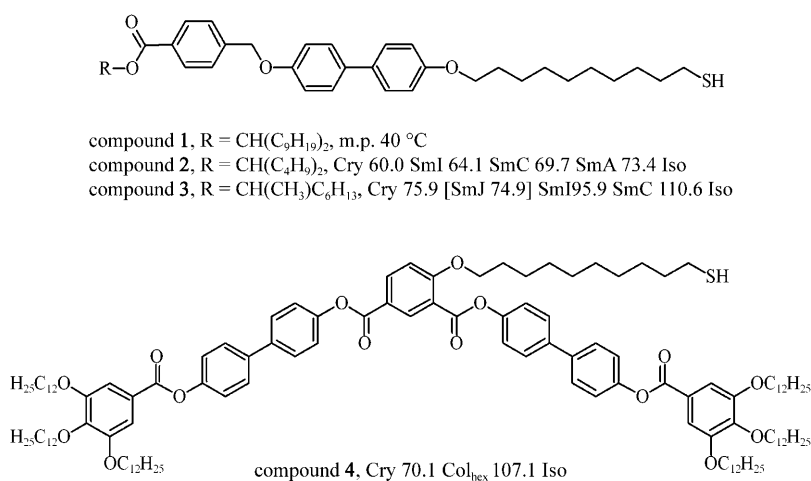
Liquid-Crystalline Phases Made of Gold Nanoparticles**

Michał Wojcik, Wiktor Lewandowski, Joanna Matraszek, Józef Mieczkowski, Jolanta Borysiuk, Damian Pocięcha,* and Ewa Gorecka

One of the great challenges in the physics and chemistry of nanomaterials is the development of efficient methods for the fabrication of ordered structures. Structured nanomaterials are desired owing to potential applications based on their unusual optical properties, such as a negative refractive index^[1] or plasmon waveguiding.^[2] The regular networks of constituents of an appropriate shape and size are usually fabricated by nanolithography;^[3] however, this method based on a top-down approach is time consuming, costly, and usually limited only to 2D structures. Thus, the development of other, bottom-up methods, in which the nanoelements self-organize spontaneously into 3D structures, is being pursued intensively.^[4]

In the case of metal nanoparticles (NPs), the most promising method is a chemical approach in which appropriate organic molecules are grafted onto a metal cluster. Such supermolecules can be described as having a rigid metallic center surrounded by a soft, deformable organic shell. Numerical simulations show that the elements, despite their spherical shape, are able to form variety of assemblies as a result of softening of the interparticle potential.^[5] Although at first glance this strategy is very attractive, in reality, owing to problems with choosing the appropriate organic coating and the nonuniformity of metal-particle size, the nanoparticles obtained yield amorphous aggregates in most cases and only occasionally form crystals with packing typical for hard spheres.^[6] It seems that to promote the formation of complex structures, the organic coating has to tune specific interactions in the system. In the last few

years, a few attempts to use mesogenic molecules for grafting onto metal clusters were motivated by the successful formation of liquid crystals from fullerene derivatives.^[7] For small gold nanoparticles, Cseh and co-workers^[8] and Kanayama et al.^[9] reported a nematic phase, whereas Donnio et al. reported a cubic phase.^[10] Herein, we show that properly functionalized NPs can exhibit smectic or columnar phases. Recently, it was predicted that such densely packed layers/columns of metallic particles are excellent candidates for future metamaterials that function at optical frequencies.^[11]



Scheme 1. Molecular structure and phase properties of mesogenic thiols used for grafting to gold clusters. Cry = crystalline, Sm = smectic, Iso = isotropic, Col_{hex} = columnar hexagonal.

Passivated gold nanoclusters were produced by the Brust–Schiffrin method^[12] with simple *n*-alkyl thiols as ligands. In a ligand-exchange reaction,^[13] the *n*-alkyl thiol molecules were then substituted by mesogenic thiols with either rodlike or bent cores (Scheme 1).

The size of the metal center, 2 nm with a distribution of 0.2 nm for all samples studied, was determined by direct TEM imaging, by X-ray scattering of a diluted NP solution, or from the Debye–Scherrer broadening of X-ray diffraction signals from the gold crystal lattice. We deduced from NMR spectroscopic and elementary analyses that approximately 65 % (for details, see the Supporting Information) of the metal surface was coated by the thiols, with the ratio of mesogenic to *n*-alkyl thiols varying from 1:2 to 1:1, depending on the reaction time for the exchange. This result indicates that between 25 and 40 mesogenic groups are attached to a single gold particle. We tested several samples to check the

[*] M. Wojcik, W. Lewandowski, Dr. J. Matraszek, Prof. J. Mieczkowski, Dr. D. Pocięcha, Prof. E. Gorecka
 Department of Chemistry, University of Warsaw
 Al. Zwirki i Wigury 101, 02-089 Warsaw (Poland)
 E-mail: pociu@chem.uw.edu.pl

Dr. J. Borysiuk
 Institute of Electronic Materials Technology
 Wolczynska 133, 01-919 Warsaw (Poland)
 and
 Institute of Experimental Physics, University of Warsaw
 ul. Hoza 69, 00-681 Warsaw (Poland)

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reproducibility of the results and found that the type of nanoparticle organization is not affected by the number of mesogenic pendants within the limits given above. The type of mesogenic molecule in the metal coating had a profound influence on gold-cluster self-assembly.

The most interesting results were obtained for particles passivated by rodlike molecules **1**, with a long, forklike end group. The 2D X-ray pattern (Figure 1) of a homogeneously

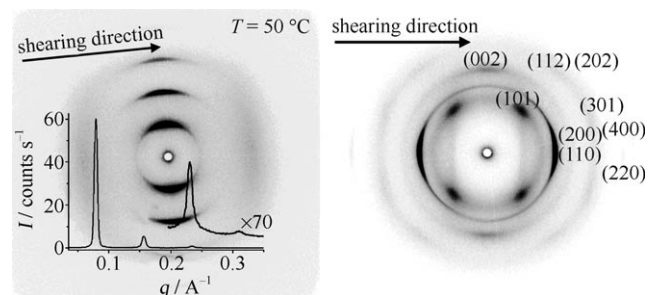


Figure 1. Left: X-ray pattern of an oriented sample of Au@1 in the smectic phase. The Bragg signals result from the layer structure, whereas the diffused signal results from the liquidlike in-plane order of gold particles inside the layers. The plot of intensity against the q vector was obtained by integration of the pattern along the azimuthal angle. Right: X-ray pattern of the columnar phase of an oriented sample of Au@2. A columnar orthorhombic body-centered lattice was chosen for indexing of the signals (see the Supporting Information).

aligned sample (with the layer wave vector oriented parallel to the substrate) shows a series of sharp Bragg reflections along the longitudinal direction and a diffused signal in the equatorial direction, and is typical for the smectic A phase.^[14] The homogeneously aligned sample with monodomains of approximately millimeter size was obtained readily by shearing a small amount of the material onto a solid (mica) substrate at a slightly elevated temperature (ca. 80°C). This technique is commonly used for the aligning of liquid crystals and results in a perpendicular orientation of the layer normal to the shearing direction. The thickness of the obtained smectic layer was approximately 8 nm, and the average interparticle distance inside the layer was approximately 3 nm. Both interlayer and inlayer periodicities were nearly temperature-independent.

This material can also be made to undergo homeotropic alignment (with the layer wave vector orientated perpendicular to the substrate) by melting of the structure on the solid substrate and subsequent fast cooling. For a homeotropic sample, up to six commensurate signals with apparatus-limited resolution were detected, which shows that the electron-density profile across the layer is strongly nonsinusoidal, as expected for layers of metal clusters separated by organic sublayers (see the Supporting Information for an electron-density profile). An X-ray rocking experiment showed that the layers can be aligned extremely well, with the layer normal orientated exactly perpendicular to the surface; the mosaicity of some samples was less than 0.1° .

The much smaller thickness of the organic sublayer (ca. 6 nm) relative to the particle distance inside the layer (ca. 3 nm) implies some redistribution of the mesogenic groups

around the metal centers (Figure 2); however, since the organic sublayer is much shorter than twice the length of the mesogenic molecule, we assume that the mesogenic cores remain orientationally and positionally disordered and prob-

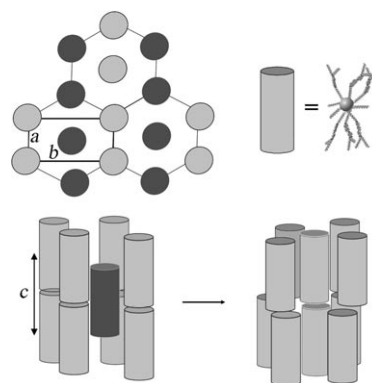


Figure 2. Schematic drawing of the arrangement of nanoparticles in the columnar phase, as viewed from above (top, left) and from the side (bottom, left); a , b , and c are the crystal-lattice parameters. A gold cluster is located at the center of each cylinder, and the cylinder is filled by orientationally and positionally disordered n -alkyl and mesogenic thiol molecules redistributed around the gold cluster. The two colors distinguish particles with their mass center (gold cluster) positioned at different levels along the c direction. Bottom: The smectic structure can be obtained from the columnar phase through movement of the particles from the intermediate layer along the column axis and decoupling of the layers.

ably partially interdigitated. The liquidlike character of the organic layer was further confirmed by the presence of a diffused signal at approximately 0.45 nm in the X-ray pattern.^[4] The orientational disorder of molecules inside the organic layer is consistent with nonmeasurable optical birefringence ($\Delta n < 0.002$) of the smectic samples. The lack of birefringence of the smectic phase described herein should not be surprising, since the birefringence of liquid crystals made of rodlike (or disklike) molecules results mainly from the orientational order of mesogenic cores.^[15] The smectic phase melts reversibly at about 110°C . In the molten state, the single diffused signal is observed at 54 \AA , which corresponds to the average distance between the particles in the short-range structure.

The type of nanoparticle lattice is altered by modification of the organic coating. The nanoparticles with the same metal centers but with ligand **2**, which has a shorter forklike tail, and with ligand **3**, which has a 2-octyl end chain, exhibit a phase in which the gold particles are arranged into columns. The structure gives rise to several incommensurate X-ray signals of a width typical for the long-range order (Figure 1). The signal positions do not correspond to either fcc or hcp lattices, which are commonly observed for the packing of hard spheres. The pattern was indexed by assuming a body-centered orthorhombic unit cell with dimensions $a \approx 83$, $b \approx 48$, $c \approx 67 \text{ \AA}$. The ratio between the a and b cell parameters ($a/b \sim \sqrt{3}$) suggests that the arrangement of particles in the ab crystallographic plane is very close to hexagonal. The presence of the signal (101), which is positioned neither along

the equatorial nor along the meridian direction, proves that the particles along the columns are positionally correlated. A body-centered orthorhombic lattice can be obtained by modification of the simple hexagonal columnar phase, that is, by shifting every second row of objects a distance half the side length of the unit cell along the column axis (Figure 2). Shifting produces vacancies in the layers of metal clusters. These vacancies are filled by the organic molecules attached to metallic cores in the layer below or above. The crystal superlattice melts reversibly at about 150 °C. If one compares the structures of the two types of materials, that is, the structures Au@2 and Au@3, which form a columnar phase, to the structure of Au@1, which forms a smectic phase, it seems that they are closely related: The smectic phase can be obtained by moving the particles along the column axis and decoupling of the obtained layers (Figure 2).

Apart from rodlike molecules, bent-core molecules **4** were tested for coating the gold clusters. Interestingly, in this case neither columnar nor smectic long-range order was found. In the small-angle X-ray pattern of the Au@4 sample, two diffused signals were registered, irrespective of sample preparation and temperature (up to the decomposition of the nanoparticles at approximately 200 °C). The ratio of signal positions ($q_1/q_2 \approx 1.6$ – 1.7) was similar to those observed for some molten metals and suggests that for the material Au@4 a possible arrangement of the particles is short-range fcc or distorted icosahedral.^[16]

In summary, chemical variation of a grafting layer formed from different mesogenic molecules can produce a variety of metal-particle assemblies. The formation of multilayer metallic-dielectric stacks (smectic phase), coupled metal wires (columnar phase), and a disordered phase confirmed the theoretical prediction^[5] that softening of the interparticle potential is sufficient for the production of different type morphologies, whereas the shape anisotropy and orientational order might be only secondary factors for nanoparticles.

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