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Control of sample alignment mode for hybrid lamellar systems based on gold nanoparticles[†]

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New hybrid materials made of gold nanoparticles functionalized by mesogenic ligands form *laminated smectic phases*. Mechanical shearing produces macro size domains with uniformly oriented layers with the layer normal either perpendicular (*perpendicular mode*) or parallel (*transverse mode*) to the shearing direction. This is in contrast to low weight and polymer liquid crystals which usually show *parallel mode* of orientation.

Achieving control over formation and alignment of single domains of soft material plays a crucial role in many advanced applications in optoelectronics and photovoltaics.^{1,2} In the case of liquid crystals (LCs) or polymers, surface treatment, flow or magnetic/electric field³ is often applied in order to align the sample. The other method, simple and low cost, is shearing of thin films of polymers or LCs. For smectic phases, made of low weight rod-like mesogens or LC polymers, shear usually aligns the smectic layer normal perpendicular to the shearing direction and along the shearing gradient (which is perpendicular to the shearing plates); such an alignment is called parallel $mode^4$ (Fig. 1a). The other observed alignment type is perpendicular mode - with the layer normal perpendicular to both: the shearing direction and the shearing gradient.⁵ (Fig. 1b). The *transverse mode*⁶ (Fig. 1c) – in which the layer normal is parallel to the shearing direction but perpendicular to the shearing gradient - has never been observed for low weight molecules as stable configuration. In the polymer LCs the transverse mode was reported only under very special conditions.^{3,5-7} Perpendicular mode is obtained because of easy sliding of the layers as it is capable of accommodating mechanical stress between layers. The parallel alignment, which also allows the sliding of layers, is favorable if the layers strongly undulate. The transverse alignment requires reduction



Fig. 1 Scheme of the alignment modes of lamellar structure: (a) parallel mode (b) perpendicular mode, (c) transverse mode. The shearing direction is along sample pulling, the shear is strong at the top of the sample and decreases inside the sample bulk thus the shear gradient is defined perpendicular to sample cover, *n* stands for the layer normal.

of layer spacing (*d*) when sheared, thus it is strongly disfavorable. Extensive studies made for polymers showed that the type of alignment is gathered largely by viscosity of the system, but also by factors like temperature, shearing strength and frequency.^{5,6,8}

In the case of structures made of hybrid nanoparticles (NPs) the large domains are usually obtained by solution-based processes such as spin coating, dip coating, or ink jet printing¹ and evaporating small molecules.⁹ The alignment by shearing was recently applied to NP materials forming liquid crystalline phases with lamellar or columnar structures,¹⁰ however there were no systematic studies on controlling the geometrical orientation of monodomains. To test the mechanism of NP-LC orientation by shearing we have synthesized hybrid materials made of gold nanoparticles covered by novel promesogenic, organic ligands. Gold nanoparticles were obtained according to the Brust–Schiffrin method¹¹ using *n*-decanethiol to passivate the metallic surface (primary grafting). The size of the particle core, 2 ± 0.5 nm, was determined by small angle X-ray scattering for particles dissolved in toluene and confirmed by analysis of the broadening of wide-angle diffraction signals related to the gold crystal lattice. Single particles contained about 315 atoms of gold¹² and approximately 95 thiol molecules at the metal surface, as confirmed by elemental analysis. No long range order was observed for gold NPs with primary grafting layers due to relatively broad size distribution of metal centers. In the

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Fig. 2 Molecular structure of ligands (L) used as a secondary grafting layer and schematic drawing of the lamellar structure built of the hybrid nanoparticles (AuL), the sublayers filled with metal and organic parts of hybrids are formed.

next step the promesogenic ligands were attached to the surface of GNPs. Three types of secondary ligands (Fig. 2) containing two rigid moieties separated by two types of long spacer (m = 4 for L1 and m = 10 for L2, L3) were used. Additionally the ligands were differed by the number (2 or 1) and length (n = 10 for L1, L3 and n = 8 for L2) of the terminal chains. For more details about organic synthesis see ESI.† Modified gold nanoparticles (AuL) were obtained *via* the Murray exchange reaction in toluene, such a method is the most often used for preparation of mesogenic NPs.^{13–17} The conditions of the reaction in all cases were the same, to ensure that the same number of the primary ligands was exchanged to the secondary ones ($\sim 50\%$).

All studied hybrid materials formed lamellar phases, with layer spacing only weakly temperature dependent; no phase transition was observed up to the clearing point (see Table 1). Similar XRD patterns were obtained for all samples: series of sharp commensurate reflections from the lamellar structure and the diffused signal (\sim 30 A) reflecting in-plane short-range positional order of metal particles. The presence of a large number of harmonics of the "lamellar" signal points to very sharp electron density modulations, with a large electron density difference between organic and metal sub-layers.^{16–18} In order to form a structure consisting of subsequent organic–metal sublayers, the secondary ligands have to be inhomogeneously distributed on the NP surface: they are placed mainly above and below the metallic core, whereas primary ligands are

Table 1 Types of ordering with average distances between layers related to temperatures for hybrid materials with the modes of alignment obtained at 40 and 80 °C. Sm stands for laminated smectic phase, Transv. – transverse mode, Perp. – perpendicular mode, II, \perp –, respectively, parallel or perpendicular orientation of the molecules to the planes made by AuNPs (see Fig. 4)

	Phase	Laver	The modes of alignment	
Comp. no	sequence [°C]	thickness, d [Å]	At 40 $^\circ \mathrm{C}$	At 80 $^\circ C$
AuL1-2 AuL1-1 AuL2-2 AuL2-1	Sm 120 Iso Sm 140 Iso Sm 120 Iso Sm 125 Iso Sm 125 Iso	95 97-102 101-102 114-120 105-107	Transv. Transv. Transv. Transv.	Perp. ∥ Perp. ∥ Perp. ∥ Perp. ⊥

distributed evenly on the core surface (Fig. 2). When studied by optical methods, materials show weak birefringence as a result of orientational order of mesogenic units. The birefringence disappears at melting temperature (Table 1). The determination of the LC sample alignment required detailed X-ray studies combined with polarized IR spectroscopy and optical microscopy for testing the orientational order of ligands. The samples were prepared by mechanical shearing of thin film of material in order to obtain large monodomains (at least a few mm size). The films were obtained by slow evaporation of solvent in which the functionalized gold nanoparticles were suspended. The shearing was made at different temperatures (with 10 degree interval, from room to isotropization temperature), the similar strength of the shearing was applied for all materials and shearing was made under static conditions. Depending on temperature a different arrangement of the layer normal with respect to the shearing direction was found (Fig. 3). At low temperatures (<60 °C) XRD patterns showed transverse mode of alignment - the layer normal was parallel to the shearing and perpendicular to the shearing gradient (Fig. 3a). The orientation was stable and the sample left even for several days at room temperature did not change the alignment. The alignment type is also independent of the used substrate: glass, polymer tapes and metal were tested. In the middle temperature range (~ 60 °C) no orientation of layers was achieved, independently of the time and strength of shearing. Materials sheared at higher temperature (>60 °C) showed XRD patterns typical for perpendicular mode, with sharp Bragg peaks along the direction perpendicular to shearing and the shearing gradient (Fig. 3b). The shearing temperature has no influence on the lamellar periodicity, the same layer spacing and the interparticle distance inside the layers were measured for samples sheared at different temperatures. The similar type of temperature dependence for alignments was observed for all materials forming lamellar NP phases (also previously synthesized by our group^{10,16-18}), so the behavior seems to be quite general. To determine the arrangement of ligand molecules in the organic sublayer the polarized IR measurements for aligned samples were performed. The anisotropy of absorption bands related to phenyl ring stretching ($\sim 1500 \text{ cm}^{-1}$) showing averaged orientation of mesogenic cores and stretching of alkyl groups ($\sim 2850 \text{ cm}^{-1}$ and $\sim 2925 \text{ cm}^{-1}$) showing averaged orientation of molecular tails was studied (Fig. 4). For the sample of AuL2-2 sheared at



Fig. 3 2D small angle XRD patterns of **AuL2-2** samples aligned by mechanical shearing at: (a) 40 °C, (b) 80 °C, with schematic drawing of layer orientation. Arrows show the shearing direction. (c) Diffracted intensity *vs.* scattering angle, obtained by integration of the pattern over the azimuthal angle. The curves are vertically shifted for clarity.



Fig. 4 The polarized IR measurements performed for **AuL2-2** samples aligned at: (a) 40 °C, (b) 80 °C and for **AuL2-1** samples aligned at: (c) 40 °C, (d) 80 °C. For more details see the main text. ϕ is the angle between the shearing direction and polarization of IR light. Arrows show the shearing direction.

low temperature the absorption for the phenyl rings was strongest in the direction perpendicular to the shearing direction (and thus perpendicular to the layer normal) while the absorption for the alkyl groups under this condition was the weakest (Fig. 4a). For the sample sheared at high temperature (80 °C) (Fig. 4b) the maximum of absorption for the phenyl ring's stretching was observed in the direction parallel to the shearing direction (which in this case was perpendicular to the layer normal) while absorption for alkyl chains was the strongest in the direction perpendicular to the shearing direction (but parallel to the layer normal) (see also ESI⁺). It proves that regardless of the temperature in which the sample was aligned, the ligand molecules remain oriented with their long axes parallel to the planes made by gold nanoparticles; the structure resembles laminated smectic phases observed for T-shaped bolamphiphiles.¹⁹ Apparently, the layer orientation drives the orientation of molecules in the organic sublayer. All synthesized NP materials showed similar behavior with exception of AuL2-1 for which ligands have only one terminal C8-alkyl chain and a long spacer unit. The sample of AuL2-1 sheared at low temperature shows transverse mode of layer alignment with ligands along the layers (Fig. 4c). However, for samples sheared at higher temperature, showing perpendicular alignment mode of layers, the strongest absorption for the phenyl rings was observed perpendicular to the shearing direction, thus along the layer normal, while the maximum of absorption for the -CH₂- groups' stretching was observed in the direction parallel to the shearing, thus perpendicular to the layer normal (Fig. 4d). This shows that ligands are on average oriented with their long axes perpendicular to layers, as in conventional smectics. Favorable formation of laminated type smectics for most

materials is probably caused by higher volume of terminal chains in comparison to the AuL2-1 having one and shortest terminal chain per ligand.

Summarizing experimental facts: depending on temperature, a different orientation of layers was induced by mechanical shearing of samples; at low temperature *transverse*, while at high temperature *perpendicular* orientation mode was observed. The polarized IR spectroscopy proved that for most materials (with one exception) mesogenic ligands in the whole temperature range follow orientation of layers, they are oriented with their long axes parallel to the planes made by gold nanoparticles. Since the ligands in *perpendicular* and *transverse* alignment modes can be either parallel or perpendicular to shearing directions it is excluded that ligand molecule orientation drives the sample (layers) alignment.

Noticeably, this is the first report on atypical alignment mode of lamellar nanoparticle systems, apparently they respond to the mechanical shear fundamentally differently than low weight LCs and block copolymers; the *parallel mode* of alignment, typical for low weight LCs and polymers, is never observed for NPs. Stability of perpendicular layer alignment mode may be understood taking into account that metal and organic sublayers are strongly coupled, as ligands are covalently attached to metallic cores. Contrary to parallel mode, the perpendicular one allows for lamellae deformation without strong distortion of the connection region between metal and organic sublayers.⁶ The stability of *transverse* alignment mode is less clear. One can argue that it is favored by growing material viscosity, as it was observed for samples sheared at lower temperatures. The presented results open up the way to prepare hybrid NP materials in the form of large-area monodomains with controlled geometrical orientation, which can be important for application in advanced optoelectronics and photovoltaics.

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