Supporting Information for *ChemPhysChem* Z721

Trapping metal nanoclusters in 'soap and water' soft crystals

Erika Eiser,* Fatima Bouchama, Mehul B. Thathagar and Gadi Rothenberg*

Experimental Section

Cross-polarised optical microscopy was performed using an Olympus BH-2 microscope coupled to a Leica DM-IRB digital camera. The gel samples were sealed two glass plates using vacuum grease to enable aging observations. Small angle X-ray scattering (SAXS) experiments were performed using a rotating anode with a copper target (λ = 1.54 Å). The distance between the sample and the detector was fixed at 1.16 m, the scattering wave vectors ranging between 0.5 nm^{-1} and 10 nm^{-1}, the instrument width being approximately 5×10^{-2} nm^{-1}. The samples were placed between two 30 μm mica sheets spaced by a glass object plate (1 mm thickness) with a window in its center and sealed with vacuum grease. X-ray exposure time was 1 h. Centrifuging was performed at 200 *g* using an Eppendorf 5412 centrifuge. Unless noted otherwise, chemicals were purchased from commercial firms (>99% pure) and used as received. Triple-distilled water was used in all experiments.

Preparation of the 'empty' (undoped) hexagonal phase. Sodium dodecyl sulphate (SDS, 0.090 mmol, 26.00 g) was mixed with water (65.00 g) at 70 ºC until a homogeneous clear solution containing SDS micelles (1:2.5 w/w SDS:H_2O) was obtained. This stock solution was used in all of the experiments. Toluene (0.16 mL, 0.14 g) was added dropwise at 50 ºC to 2.50 g of this stock solution to swell the micellar phase. Then, the cosurfactant 1-pentanol (0.13 mL, 0.11 g) was added dropwise to the swollen micellar phase to give a clear gel of hexagonally ordered wormlike micells.

The doped hexagonal phase was prepared using the same procedure as above except that an equivalent amount of toluene containing the stabilized metal nanoclusters was used.

Synthesis of the metal nanoclusters. Example: palladium nanoclusters isolated and redispersed in toluene. A Schlenk-type vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N_2. $PdCl_2$ (0.2 mmol, 35.4 mg), tetraoctylammonium bromide (TOAB, 0.2 mmol, 109.3 mg) and toluene (50 mL) were injected into the vessel and 0.25 mL of 26.0 mM aqueous $NaBH_4$ was added dropwise over 1 h to reaction mixture at 20 ºC. The mixture was stirred for another 2 h to obtain the clusters as a black suspension in the toluene phase. The phases were then separated and the toluene phase containing the clusters was dried under vacuum (0.1 KPa, 40 ºC) to give the clusters as a dry black powder. The clusters were then weighed and re-dispersed in an exact volume of toluene to give the desired concentration.

Nanocluster suspensions of Au, Ag, Ru and Cu were prepared in a similar manner using $HAuCl_4$, $AgNO_3$, $RuCl_3$, and $CuCl_2$ as presursors. The suspensions were prepared in concentrations of 0.030 M, 0.075 M, and 0.15 M.

Notes on interpretation of SAXS and microscopy experiments

SAXS measurements. The scattering pattern of a hexagonal phase exhibits 2 Bragg peaks with position ratios 1:√3. The position of the first peak q_0 is related to the distance between the centers of adjacent tubes, d, through $d = \frac{2\pi}{\sqrt{3}} \times \frac{2}{q_0}$. Using geometrical considerations, we can relate the tube radius R to the lattice parameter d and the volume fraction of the polar medium ϕ_p (eq S1, where ϕ_p includes the water and the polar 'heads' of surfactants and co-surfactants).[1] There is an aqueous layer between the tubes of width l, where $l = d - 2R$. Substracting the layer of the hydrophilic SDS head-group (about 0.6

(1). *Cf.* with Ramos, L.; Fabre, P.; Ober, R. *Eur. Phys. J. B,* **1998**, *1*, 319–326, who suggest a separation between rods of ~1.5 nm.

nm) we estimate the volume fraction of the organic (nonpolar) medium to be $\phi_o = 1 - \phi_p \approx 0.61$, and obtain $l \approx 1\,\text{nm}$.

$$R = d\,\frac{\sqrt{3}}{2\pi}\sqrt{(1-\phi_p)} \qquad \text{(S1)}$$

In general, three geometries can be envisaged for lyotropic hexagonal phases: *(i)* direct (nonpolar tubes in a polar medium); *(ii)* inverse (polar tubes in a nonpolar medium); and *(iii)* complex (a bicontinuous phase). A detailed study of the shape factor of the scattering spectra can give indications on the nature of the phase. This method is not specific enough for unambiguous determination of the phase's nature, but it does indicate, for all three hypotheses, the size of the lyotropic elements.

Cross-polarised micrographs. The doped quaternary system shows the existence of birefringent phases whose texture are characteristic of a hexagonal phase. The observed texture between the crossed polarizers that forms spontaneously between the plane glass boundaries is commonly referred to as fan-shaped.[2] It indicates that the tubes orient parallel to the glass plates, which can be explained in terms of an anchoring energy. However, the orientation of the tubes that locally defines the optical axis is two-fold degenerate in the plane, giving domains of different orientations observed in the fan shaped texture. The presence of striations (the thin stripes) is a positive identification of the hexagonal phase. These striations, typical of a hexagonal phase, are due to a slight cooperative undulation of the lyotropic tubes. The average orientation of the tubes is perpendicular to the striations.

([2]). Livolant, F.; Bouligand, Y. *J. Physique,* **1986**, *47*, 1813–1827.