

SUPPLEMENTARY INFORMATION – Fong et al.

Materials & Methods

Materials: Phytantriol (3,7,11,15-tetramethyl-1,2,3-hexadecanetriol) was a gift from DSM (Basel, Switzerland). Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium borohydride (NaBH_4), silver nitrate, ascorbic acid, cetyltrimethylammonium bromide (CTAB) and dodecanethiol were obtained from Sigma-Aldrich (St Louis, MO) and used as received. Polyethyleneglycol thiol (PEG-SH, Fw 5000) was obtained from Rapp Polymere (Tübingen, Germany).

Gold nanorods synthesis: Gold nanorods with longitudinal surface plasmon resonances at 810 and 660 nm were prepared using the standard seed-mediated growth methodology in presence of cetyltrimethylammonium bromide (CTAB). The aspect ratio of the nanorods was controlled through control of the silver nitrate concentration as described. [1] The gold nanorods were hydrophobized using the alkanethiol dodecanethiol in a two-step ligand exchange procedure as previously described [2]. Briefly, the as synthesized gold nanorods were first purified to remove the excess CTAB molecules and an intermediate steric barrier was introduced using a thiol-terminated polyethylene glycol (PEG-SH). The second step of the process involved the removal of the residual CTAB bilayer and the ligand exchange of the PEG-SH molecules by dodecanethiol. **The hydrophobized gold nanorods could be readily redispersed in non-polar solvent (e.g. chloroform, tetrahydrofuran) and remained stable for several hours. The UV-vis absorption spectra of the as synthesized and hydrophobized gold nanorod suspensions with a LSPR at 810 nm are presented in Figure SI 1. No broadening of the absorption spectra was observed for the gold nanorods redispersed in non-polar solvents, confirming the absence of significant aggregation during the ligand exchange procedure. Although the gold nanorods polydispersity index has not been directly calculated in this study, the samples dispersity was in good agreement with previously published gold nanorods dispersion prepared using the standard CTAB - seed-mediated growth methodology as indicated by TEM size measurements (Average aspect ratio: 3.3; Length: 55.5 +- 9.5 nm, Width: 16 +- 2.5) and width of the longitudinal surface plasmon resonance absorption spectrum.**

Liquid crystalline formulations: Formulations were prepared by dissolving phytantriol in THF and mixing with the gold nanorod suspension in THF in appropriate quantities. The THF was removed *in vacuo* and an equal weight of water added to the phytantriol + gold nanorods mixture to form the liquid crystalline phase (50% w/w water is in the excess water region of the phase diagram for the phytantriol-water system [3]). The mixture was mixed by heating to 70°C momentarily to reduce viscosity and allow vortex mixing, and allowed to equilibrate for 48 hr at room temperature prior to investigation. The sample (50 mg) was sandwiched between Kapton tape and mounted on a hot stage to control temperature for temperature scans and at 30°C for laser irradiation studies.

Small angle x-ray scattering: Temperature scan SAXS experiments were performed at ANSTO, NSW, Australia, on a Bruker Nanostar SAXS camera, with pinhole collimation for point focus geometry. The instrument source was a copper rotating anode (0.3 mm filament) operating at 45 kV and 110 mA, fitted with cross-coupled Montel mirrors, resulting in $\text{CuK}\alpha$ radiation wavelength 1.54 Å. Dynamic SAXS data were collected on the SAXS instrument at the Australian Synchrotron [4]. An X-ray beam with a wavelength of 0.83 Å (15 keV) was selected. The 2D SAXS patterns were collected using a Pilatus 200k detector (active area $169 \times 33 \text{ mm}^2$ with a pixel size of 172 μm) which was located 966 mm from the sample position. This geometry enables a d-spacing in the range of 350 to 5 Å (i.e. molecular dimensions) to be studied. The d-spacing is derived from Bragg's law ($\lambda = 2d \sin \theta$; where λ is the wavelength of the incident radiation, and 2θ is the scattering angle) and is

inversely related to the scattering vector, q ($q = 4\pi \sin \theta/\lambda$). The q is, in turn, related to the position of the scattered X-ray on the 2D detector with $q = 0 \text{ \AA}^{-1}$ at the centre of the detector. The total q range for the instrument configuration outlined above was $0.02 < q < 1.06 \text{ \AA}^{-1}$. 2D SAXS patterns were collected for 100 ms over 30 sec; the computer software SAXS15ID [5] and Fit2D [6] were used to acquire and reduce 2D patterns to 1D curves.

The NIR light source used in these experiments was a Class IIB diode laser with the output $\lambda = 808 \pm 3 \text{ nm}$ and peak power $< 400 \text{ mW}$ (Changchun New Industries, China). Samples were illuminated by computer controlled pulses with an unmodified laser beam.

[1] B. Nikoobakht and M. A. El-Sayed, *Chem. Mat.*, 2003, **15**, 1957-1962.

[2] Thierry, B., et al. A robust procedure for the functionalization of gold nanorods and noble metal nanoparticles. *Chem Comm*, 1724-1726 (2009).

[3] Dong, Y-D. et al. *Langmuir* 2008, **24**, 6998-7003.

[4] <http://www.synchrotron.org.au/index.php/aussyncbeamlines/saxswaxs/saxs-specifications>

[5] <http://www.synchrotron.org.au/index.php/aussyncbeamlines/saxswaxs/saxs-data-a-processing>

[6] Hammersley, A. P. ESRF Internal Report, ESRF98HA01T 1998, FIT2D V9.129 , Reference Manual V3.1.

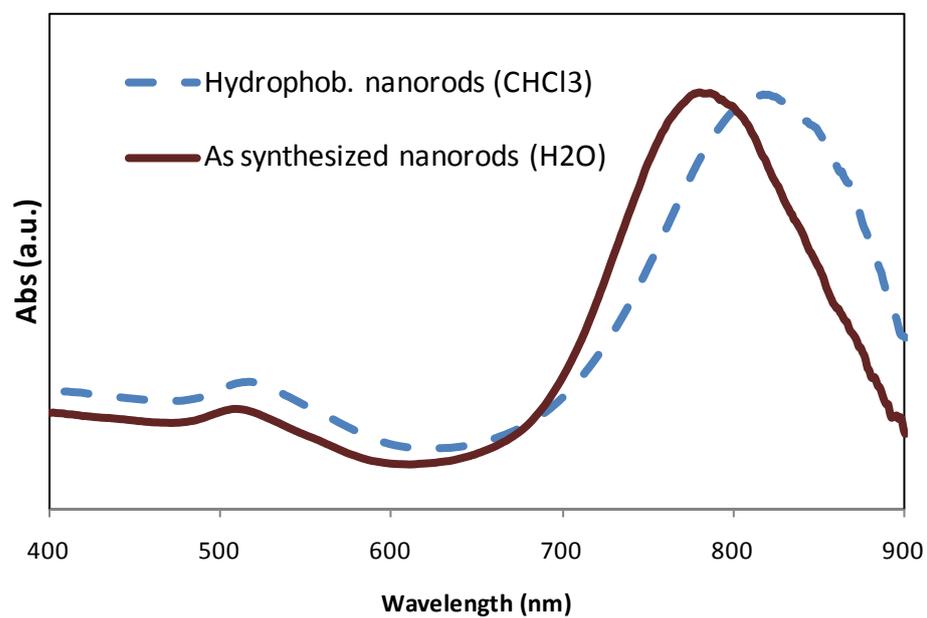


Figure SI 1. Normalized absorption spectra of the as synthesized gold nanorods (CTAB capping, H₂O) and dodecanethiol hydrophobized gold nanorods (in Chloroform).

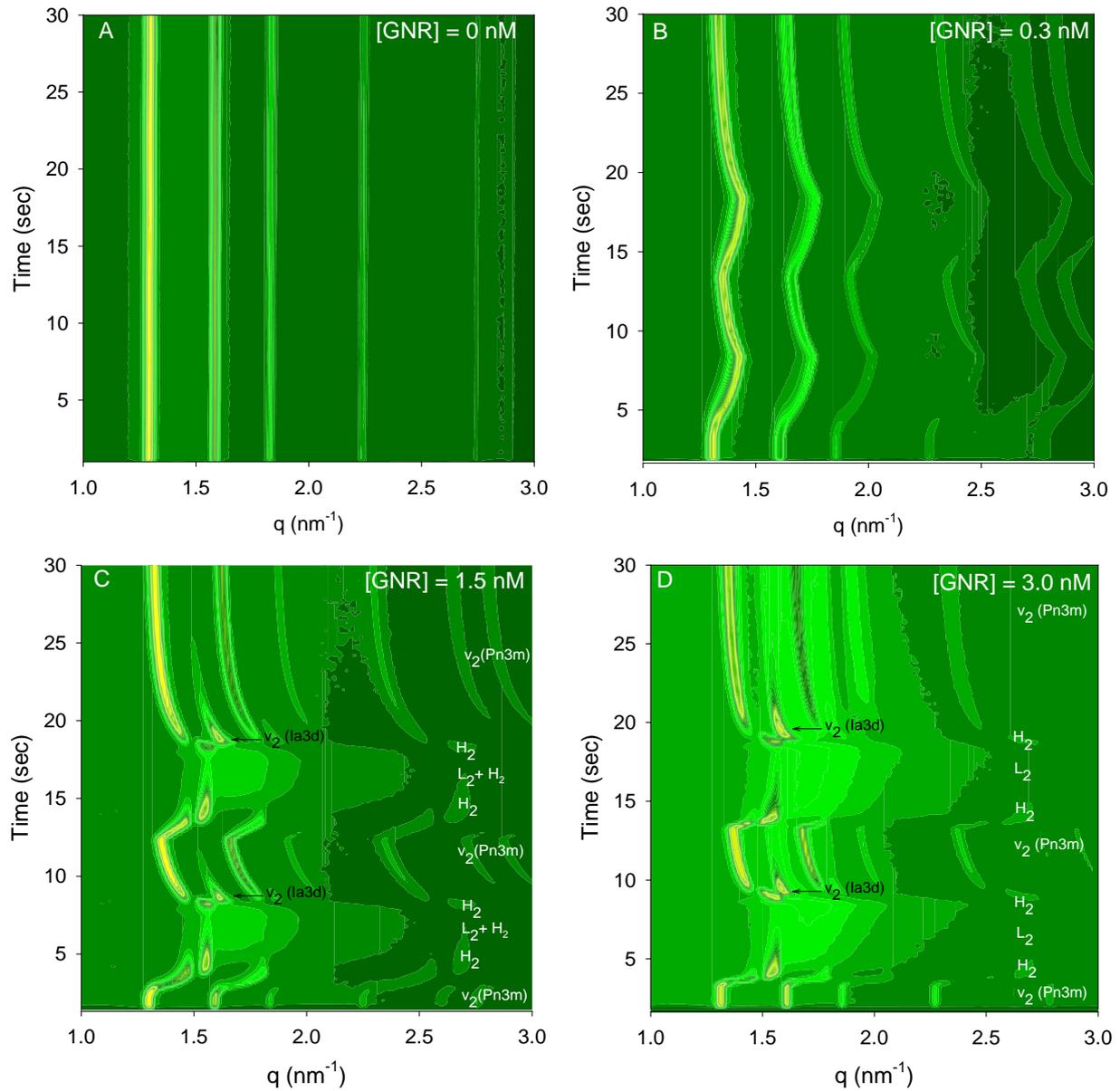


Figure SI 2 - Time resolved synchrotron small angle x-ray diffraction profiles for the phytantriol + water system with increasing concentration of gold nanorods (GNR). Laser sequence started with 2 sec wait to allow determination of initial equilibrium phase structure, then 5 s on, 5 s off, 5 s on and 13 s off. Increased colour intensity towards bright yellow indicates increased intensity of signal at that q -value. Annotated phase structures determined from indexing peaks in intensity vs. q profiles from individual frames. See text for description of individual phase notation.