## ELECTRONIC SUPPLEMENTARY INFORMATION

# Scanning Tunneling Microscopy and Small Angle Neutron Scattering Study of Mixed Monolayer Protected Gold Nanoparticles in Organic Solvents.

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# **1. EXPERIMENTAL SECTION**

### 1.1. Nanoparticles synthesis.

0.25mMol chloro(triphenylphosphine)gold was dissolved in 20mL of benzene and 0.5mMol of ligands (with the different ratios) were added and left to mix for 10 min. After that 2.5mMol of a borane tert-butylamine complex dissolved in 20mL of benzene was added to reduce the sample. Once mixed the solution was put immediately to reflux and left to react for one hour in strong stirring. The sample was precipitated with methanol and the purification was made in several cycles of centrifugation with methanol and acetone.

# 1.2 Ligand ratio determination.

The purity of the NPS was initially checked with <sup>1</sup>H NMR. After the 5<sup>th</sup> cleaning, the absence of sharp peaks was a good indicator of the cleanness of the nanoparticles.

To characterize the ligand ratio an amount of NP between 5 to 10mg was added to a vial together with 0.7mL of CD<sub>3</sub>OD and around 10 mg of KCN (KCN has proved to be a good etching agent on gold surfaces<sup>1</sup> and nanoparticles<sup>2</sup>) The sample was sonicated to disperse the nanoparticles and left until the solution became totally transparent. <sup>1</sup>H NMR was performed directly on that solution (Fig. S1).

The ligand ratio was obtained by comparing the peak between 0.8 and 1ppm that corresponds to the terminal  $CH_3$  of both molecules with the peaks between 1.2 and 1.75 that corresponds to the  $CH_2$  except the ones close to the sulfur (20 protons for DDT and 8 for HT). The  $CH_2$  close to the sulfur group appears region 2.4 to 3.1 that is shown as different peaks due to the presence of disulfides and

thiols in the solution and possibly to the interaction with the KCN. Results of the ligand ratio appear in the table S1.

# 1.3. Nanoparticle size determination using TEM images

TEM images were taken in a Philips/FEI CM12 operating at 100 kV. The images were analyzed using the Image J software package [http://rsbweb.nih.gov/ij/]. The default threshold was used and the diameter was calculated from the area assuming the particles were spherical. At least 500 particles were counted on images of different areas of the grid to obtain significant statistics (Fig. S2).

Table S1. Size, size distribution and ligand shell composition as determined by TEM and  $^1\!\mathrm{H}\,\mathrm{NMR}.$ 

	Diameter (Å)	Polydispersity (Å)	<sup>1</sup> H NMR composition	
C6: C12	49	6	C6 fraction=0.2	
			C12 fraction=0.8	
d-C6: C12	49	4	*	
C6: d-C12	48	4	*	

\*Similar composition for the ligand shell composed of deuterated ligands is expected, as the deuterium substitution does not affect the chemical properties of the molecule.

# 1.4. STM samples preparation.

A solution of nanoparticles in toluene was deposited on the water subphase of a Langmuir trough. The nanoparticle sample in gas phase was left for 10 minutes to obtain complete evaporation of the solvent and after that the layer was compressed until it reached the solid phase. The nanoparticle monolayer was then transferred to a gold on mica substrate using a Langmuir Schaefer method. Figure S3 shows a monolayer of nanoparticles after being transferred to a carbon coated grid.

2. Determination of nanoparticles size and concentration using Small-Angle X-ray Scattering (SAXS)

Small Angle X-ray Scattering (SAXS) curve was obtained on an S-Max 3000 instrument (Rigaku, Innovative Technologies, Auburn Hills, USA) which uses three pinholes (PH) to collimate the beam (high resolution configuration: PH1 = 0.4 mm, PH2 = 0.2 mm, PH3 =0.7 mm). To increase the q-range, the system was used in an off-set configuration where the incident beam does not hit the centre of the two-dimensional multiwire gas detector. Absolute calibration of the instrument was performed using the procedure reported in the literature<sup>3</sup>. The

same C6-dC12 nanoparticle chloroform solution used for collecting SANS profile was also measured using SAXS. The measured two-dimensional SAXS pattern was normalized to an absolute scale, azimuthally averaged, and background subtracted to obtain the scattered, I(q), as a function of scattering vector q. The profile obtained was then fitted using Irena software<sup>4</sup>. A model scattering function based on Gaussian distribution of gold spheres with a mean size value of 48 Å is the best fit to the experimental data, with a standard deviation of 4 Å. These values are in good agreement with the results obtained using TEM. Using the same Irena software we determined a volume fraction of 1.6  $10^{-4}$ [2] for the nanoparticle solution. The dC6-C12 solution was not measured but we assumed the same volume fraction for this solution too. We believe that this is a valid assumption given that the size of the dC6-C12 particles was found (via TEM) to be exactly the same than the C6-dC12 particles and we could not detect any differences in solubility between these two particles.

# 3. SANS

SANS measurements were conducted on the KWS-2 beamline at the Julich Center for Neutron Science at the FRM-II reactor, TU, Muenchen. Measurements were performed at room temperature, using 1.05 m sample-to-detector distance, at 5 Å wavelength with a collimation setup of 8 m. The samples were measured at a volume fraction of gold nanoparticles of  $1.6 \ 10^{-4}$ . The two-dimensional scattering data was azimuthally averaged, background subtracted, corrected for empty cell and sample transmission, and established on an absolute scale. The scattering length density (SLD) used in the SANS modeling are reported in table S2.

Table S2. Scattering length values used in the SANS modeling.

	d-DDT	h-DDT	h-HT	d-HT	Gold
SLD (Å <sup>-2</sup> )	5.6 10 <sup>-6</sup>	$-2.7 \ 10^{-7}$	-2.6 10 <sup>-7</sup>	5.0 10 <sup>-6</sup>	4.5 10 <sup>-6</sup>

# 4. Calculation of SANS intensity

We report the details of calculating the scattering intensity from a Dummy Atom Model (DAM) used for the fitting. Denoting the contrast of the beads in the *k*-th phase as  $\Delta \rho_k$ , the scattering intensity from the entire DAM is

$$I(q) = \left\langle \sum_{k=1}^{K} \Delta \rho_k A_k^2(\mathbf{q}) \right\rangle_{\mathcal{Q}}$$
(1)

where  $A_k(\mathbf{q})$  is the scattering amplitude from the volume occupied by the *k*-th phase and K is the number of phases (here, K=2). The scattering amplitudes are conveniently represented as

$$I(q) = 2\pi^{2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left\{ \sum_{k=1}^{K} \left[ \Delta \rho_{k} A_{lm}^{(k)}(q) \right]^{2} + 2 \sum_{n>k} \Delta \rho_{k} A_{lm}^{(k)}(q) \Delta \rho_{n} \left[ A_{lm}^{(n)}(q) \right]^{*} \right\}$$
(2)

Here, the partial amplitudes from the volume occupied by the *k*-th phase in a DAM are rapidly evaluated from the bead positions using spherical harmonics  $Y_{lm}(\omega)$  as

$$A_{lm}^{(k)}(q) = i^{l} \sqrt{2/\pi} v_{a} \sum_{j} j_{l}(qr_{j}) Y_{lm}^{*}(\omega_{j})$$
(3)

where the sum runs over all atoms of that phase,  $(r_j\omega_j) = r_j$  are their polar coordinates and  $v_a = (4\pi r_0^3/3)/0.74$  is the displaced volume per dummy atom. Eqs. (1-3) allow one to rapidly compute the scattering curves from a multiphase DAM for an arbitrary configuration *X* and arbitrary contrasts  $\Delta \rho$ .

#### 5. Image processing/PSD

STM images were simulated using the following apprach. After importing the PDB file into the Blender 3D graphics software (Blender Foundation), all scattering entities except for those corresponding to the C6 phase, were removed. The scattering entities corresponding to the metal core were replaced with a sphere of equivalent diameter. This adapted nanoparticle structure was then duplicated and arranged into a quasi-hexagonal array, in which each nanoparticle was given a random three-dimensional orientation.

An image was generated by adapting the "composition nodes" within Blender to generate a greyscale image in which the absolute distance from the virtual camera yielded a corresponding greyscale value, with lighter colors corresponding to shorter distances. The virtual camera was set to render orthogonally. The rendered image was passed through a sliding paraboloid rolling ball filter in ImageJ (National Institutes of Health, Bethesda, USA).



Figure S1: 1H NMR spectrum of C12:C6 2:1 nanoparticles in deuterated methanol after the etching of the gold core.



**Figure S**2. TEM image of C12:C6 2:1 nanoparticles. Inset show the histogram of the size distribution for the particles.



Figure S3. TEM image of a Langmuir-Blodgett film of nanoparticles.



**Figure S4.** STM images of the C12: C6 sample. Trace (a), current (b) and retrace (c) scans of the STM image recorded at scanning angle of  $30^{\circ}$ . Bias  $V_b = 1500 \text{ mV}$  and tunneling current  $I_t = 300 \text{ pA}$ .



**Figure S5.** STM images of the C12: C6 sample. Trace (a), current (b) and retrace (c) scans of the STM image recorded at scanning angle of  $60^{\circ}$ . Bias  $V_b = 1500 \text{ mV}$  and tunneling current  $I_t = 300 \text{ pA}$ .



**Figure S6.** STM images of the C12: C6 sample. Trace (a), current (b) and retrace (c) scans of the STM image recorded at scanning angle of 90°. Bias  $V_b = 1500$  mV and tunneling current  $I_t = 300$  pA.



**Figure S7.** STM images of the C12: C6 sample. Trace (a, d), current (b, e) and retrace (c, f) scans of the STM image recorded at scanning angle of  $0^{\circ}$  before (a, b, c) and after a full rotation (d, e, f). Bias V<sub>b</sub> = 1500 mV and tunneling current I<sub>t</sub> = 300 pA.



**Figure S8.** This is the same figure shown in the main text as Figure 3 with all of the markings removed but the scan line used to produce Figure 3f. Additionally image **f**) shows line profiles along the direction indicated by number 2 in images **a** and **b**.



**Figure S9**: UV-Vis spectrum of C12-C6 nanoparticles in 1-phenyloctante (after two days in solution) showing a surface plasmon resonance peak at  $\sim$ 550 nm. This value probably indicates the presence of some aggregates of particles in the solution.



**Figure S10.** STM images recorded in air of the C12: C6 sample. The hexagonal packing is evident from the image, likely due to low polydispersity of the particles and to the sample preparation. The feature, at ~ 1 nm, is barely distinguishable. Trace (a), current (b) and retrace (c) scans of the STM image recorded at scanning angle of  $0^{\circ}$ . Bias  $V_b = 1000 \text{ mV}$  and tunneling current  $I_t = 500 \text{ pA}$ .



**Figure S11**. PSD plots of four STM topography images of the C12:C6 sample acquired at different tip speeds. The plot in (a) is shown as a function of the spatial wave-vector k, while that in (b) is shown as a function of the temporal frequency  $\omega$ . The legend within the figure denotes the tip velocities. It should be immediately evident that the plot overlap remarkably well in spatial coordinates but space out when replotted in temporal coordinates indicating that the images are due to true tip-sample interactions.



**Figure S12**. 2D FFT of image a shown in Figure 1 on the main text. No major features can be observed.



**Figure S13**. Difference image of the images Figure 1a and 1b in the main text.



Figure S14. PSD plots of all the images presented in Figure 2.

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**Figure S15.** (a) SANS graphs recorded for the C6: d-C12 and d-C6: C12 particles on diluted solutions in deuterated chloroform (C6: d-C12 red circles and d-C6: C12 blue triangles). These are the same experimental points shown in Figure 4 of the main text. The solid lines correspond to the fit. The model fit in the graph is obtained imposing a Janus configuration to the shell of nanoparticles.

(b), Projection of the multiphase 3D low-resolution model of the C6: C12 particles in Janus configuration of the ligand shell. Yellow beads indicate the gold nanoparticle core regions, the magenta beads represent the C6 moiety, and the cyan beads the C12 moiety. The beads in the model act as low-resolution placeholders to depict the space occupied by the gold, C6 and C12 moieties. The transparency of cyan and magenta beads was used to better represent the particle.

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**Figure S16.** (a) The SANS graphs recorded for the C6: d-C12 and d-C6: C12 particles on diluted solutions in deuterated chloroform (C6: d-C12 red circles and d-C6: C12 blue triangles). These are the same experimental points shown in Figure 4 of the main text. The solid lines correspond to the fit. The model fit is obtained imposing a uniformly mixed configuration to the shell of nanoparticles. (b) Projection of the multiphase 3D low-resolution models of the C6: C12 particles in uniformly mixed configurations of the ligand shell. Yellow beads indicate the gold nanoparticle core regions, the magenta beads represent the C6 moiety, and the cyan beads the C12 moiety. The beads in the model act as low-resolution placeholders to depict the space occupied by the gold, C6 and C12 moieties. The transparency of cyan beads was used to better represent the uniformly mixed morphology of the magenta beads.



**Figure S17.** Grey scale image obtained by assembling together many projections of the same 3D low-resolution model obtained as a best fit for the SANS data. The particles image present bright and less bright features as in the model some C6 domains are further away from the gold phase than others. This is due to the intrinsic low resolution of the model used.

- 1. Kumar, A., Biebuyck, H.A., Abbott, N.L. & Whitesides, G.M. The Use of Self-Assembled Monolayers and a Selective Etch to Generate Patterned Gold Features. *J. Am. Chem. Soc.* **114**, 9188-9189 (1992).
- 2. Templeton, A.C., Hostetler, M.J., Kraft, C.T. & Murray, R.W. Reactivity of monolayer-protected gold cluster molecules: Steric effects. *J. Am. Chem. Soc.* **120**, 1906-1911 (1998).
- 3. Fan, L., Degen, M., Bendle, S., Grupido, N. & Ilavsky, J. The Absolute Calibration of a Small-Angle Scattering Instrument with a Laboratory Xray Source. *Journal of Physics: Conference Series* **247**, 012005.

4. Ilavsky, J. & Jemian, P.R. Irena: tool suite for modeling and analysis of small-angle scattering. *Journal of Applied Crystallography* **42**, 347-353 (2009).