Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Tuneable 2D self-assembly of plasmonic nanoparticles at liquid | liquid interfaces

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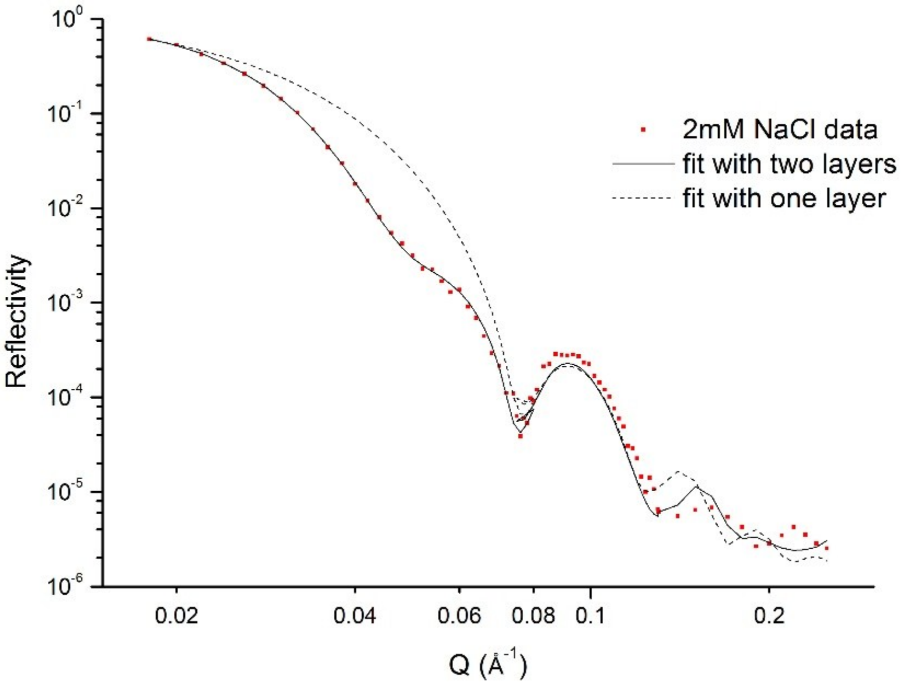
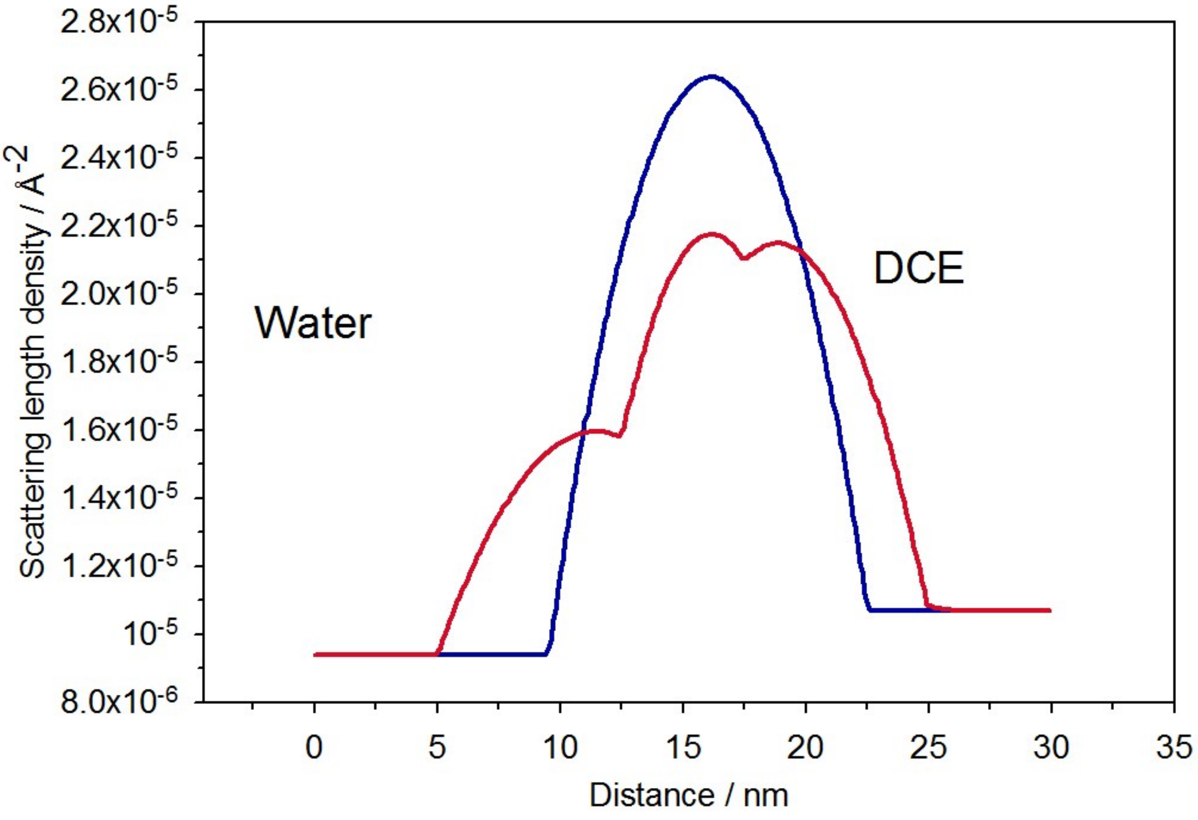
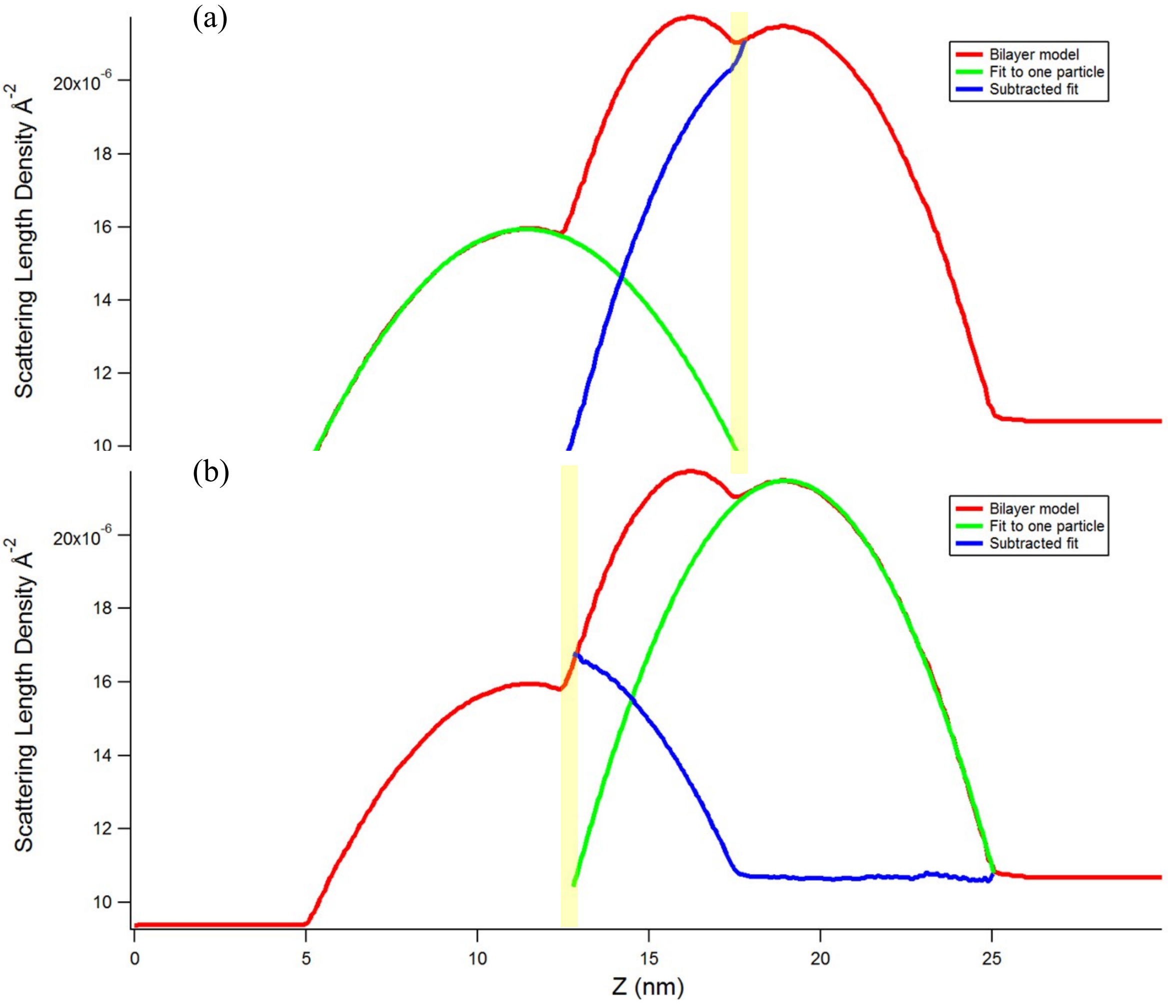
X-ray reflectivity



SI Figure 1. X-ray reflectivity curve for gold NPs assembled at the water – DCE interface with 2 mM NaCl. The data is fit with a two layer and one layer model.



SI Figure 2. Scattering length density plot for single and two layers for 2mM NaCl. The two layer plot sums up the individual layer densities, resulting in a triply peaked profile. The triply peaked profile can also be reproduced if a minimum of four layers is used model is allowed to fit the data. This is however very computationally intensive, has 12 sample variables and *per se* offers no insights into the material structure at the LLI.



SI Figure 3. If one of the particles in the bilayer model is fit and subtracted from the model, a sharp increase (a) or a decrease (b) is seen in the scattering length density. This arises due to the density difference between the two phases, which suggests that the interface exists between (a) and (b) (between 12.5 and 17.5 nm above).

SI Table 1. X-ray reflectivity measurements showing parameters for NP layers assembled at the water – DCE interface with **NaCl in the aqueous phase**.

[NaCl]/mM	NP diameter/ nm	NP coverage	Displacement /nm	Fraction in layer	χ^2	Recalculated NP coverage at GID hcp
1	13.34±0.82	0.09±0.03	9.79±3.43	0.28±0.02	4.3	0.17±0.05
2	12.34±0.74	0.26±0.02	7.40±1.25	0.36±0.01	3.5	0.34±0.02
5	12.24±0.42	0.25±0.02	8.03±1.55	0.38±0.01	13.7	0.34±0.02
8	12.92±0.42	0.27±0.02	7.51±1.55	0.21±0.01	2.3	0.36±0.02
10	12.76±0.12	0.29±0.01	8.44±3.20	0.30±0.01	8.0	0.37±0.01
12	12.86±0.52	0.36±0.02	4.82±2.71	0.48±0.02	211	0.45±0.02
15	12.44±0.16	0.33±0.01	7.15±1.05	0.81±0.01	14.6	0.43±0.01
17.5	12.16±0.16	0.31±0.01	5.66±1.35	0.78±0.01	7.1	0.40±0.01
25	12.14±0.16	0.37±0.01	5.66±0.82	0.83±0.01	3.7	0.50±0.02
35	12.84±0.06	0.65±0.02	5.93±1.13	0.82±0.02	46.8	0.81±0.02
50	12.98±0.08	0.80±0.01	5.71±0.82	0.93±0.01	8.4	0.93±0.02
75	12.34±0.08	0.72±0.01	1.37±2.55	0.92±0.01	15.6	0.94±0.01
100	12.8±0.08	0.81±0.01	6.56±0.05	0.96±0.01	47.6	1.00±0.01

SI Table 2. **X-ray** reflectivity measurements showing parameters for NP layers assembled at the water – DCE interface with **TBA TPB in the organic phase**.

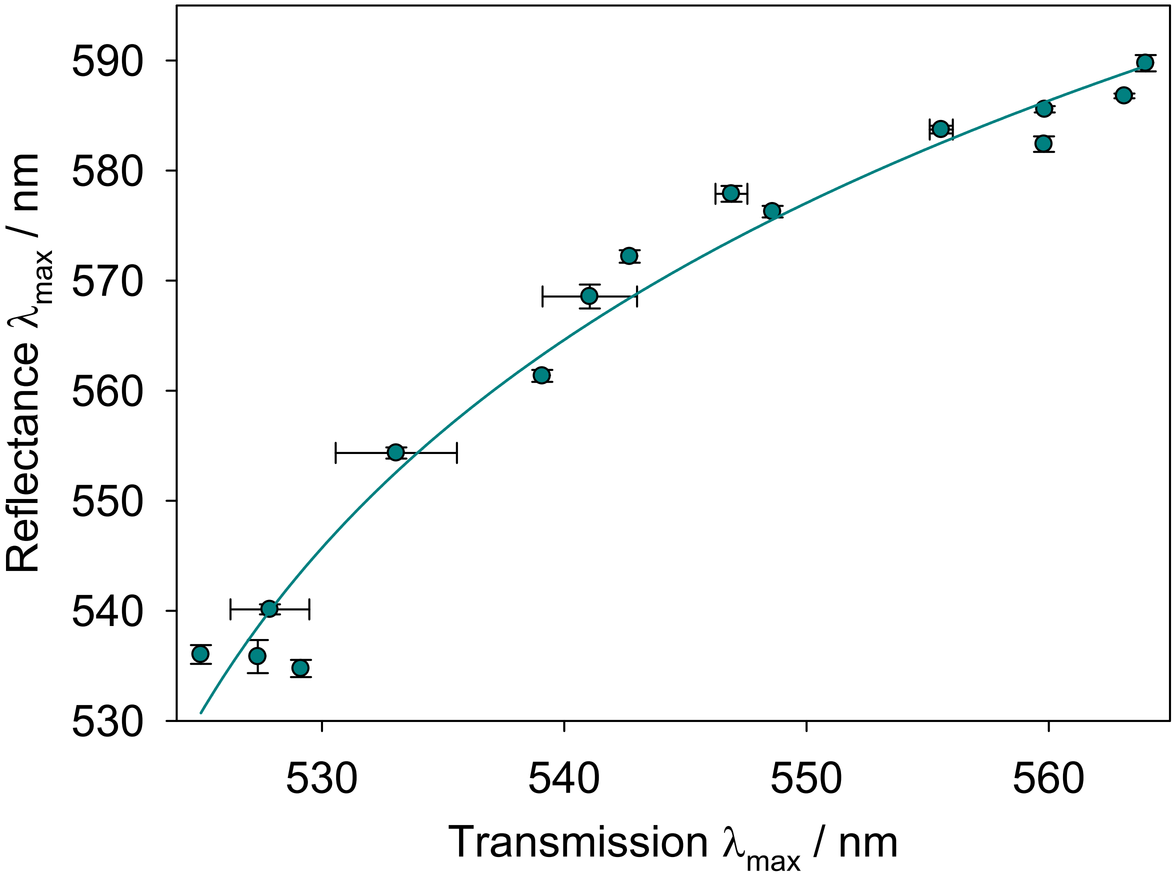
[TBATBP]/mM	NP diameter/nm	NP Coverage	Gaussian spread/Å	χ^2	Recalculated NP coverage at GID hcp
1	13.6±0.12	0.08±0.01	8.6±5.5	14.4	0.09±0.01
2	13.24±0.12	0.40±0.01	4.5±1.2	4.7	0.51±0.01
4	13.38±0.02	0.48±0.01	1.7±0.1	11.6	0.60±0.01
8	12.64±0.06	0.69±0.01	4.1±0.5	37	0.95±0.01
10	13.22±0.02	0.62±0.01	4.1±0.5	6.5	0.79±0.01

Further discussion of XRR and diffraction results

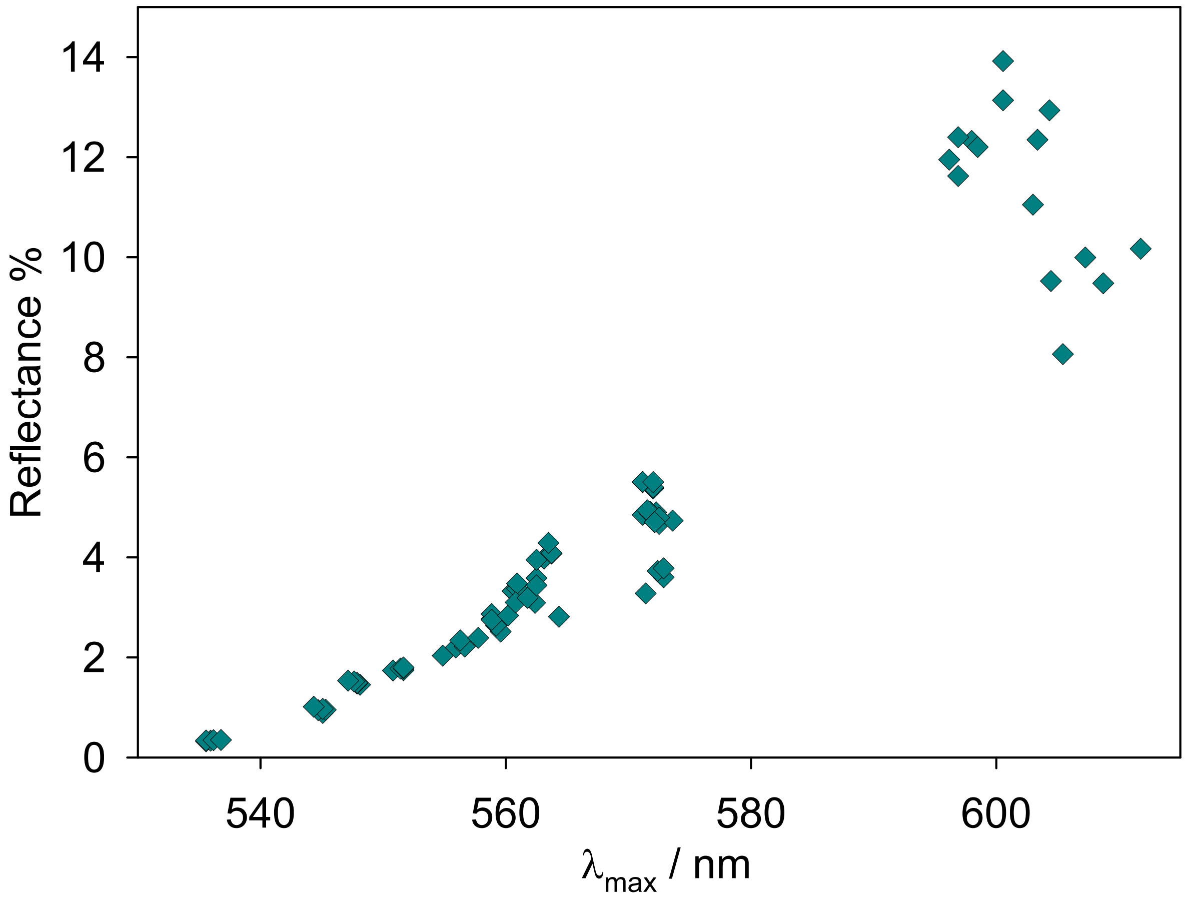
The diameter initially used to calculate the coverage of NPs directly from the reflectivity is that from the TEM measurements plus the thickness of the adsorbed MDDA layer; (12.8 nm + 2x1.5 nm) (Figure 1 b). We know the effective electron density of the layer, and assuming hexagonally close packed (hcp) NPs of total diameter 15.8 nm, we can calculate an initial coverage which comes out below a monolayer at all concentrations (SI Table 1 & 2, "NP Coverage"). The GID then measures the d-spacing of the 2-d layer in the plane. This is model independent at 15.3 nm. If the NPs are chosen to be hcp, then you can calculate a centre to centre distance, which is found to limit at 17.6 nm (2*d-spacing/ √3) for NaCl higher concentrations. If 17.6 nm is chosen as the limiting close-packed separation and the reflectivity is refitted, the only thing that changes is the coverage – which now tends to 1 at the highest concentrations (SI table 1 & 2, "NP coverage at GID hcp"). What this means is the surface is fully covered by NPs (of diameter 15.74 nm) which each occupy an area with diameter 17.6 nm.

In the absence of higher order Bragg peaks it is impossible to suggest, for example, that the two-dimensional lattice is cubic rather than hexagonal close packed, and so whether the NPs are genuinely close-packed. Earlier results however Kim et al.[1] showed higher order GID peaks which demonstrated that the same NPs did indeed form hcp layers at the liquid interface.

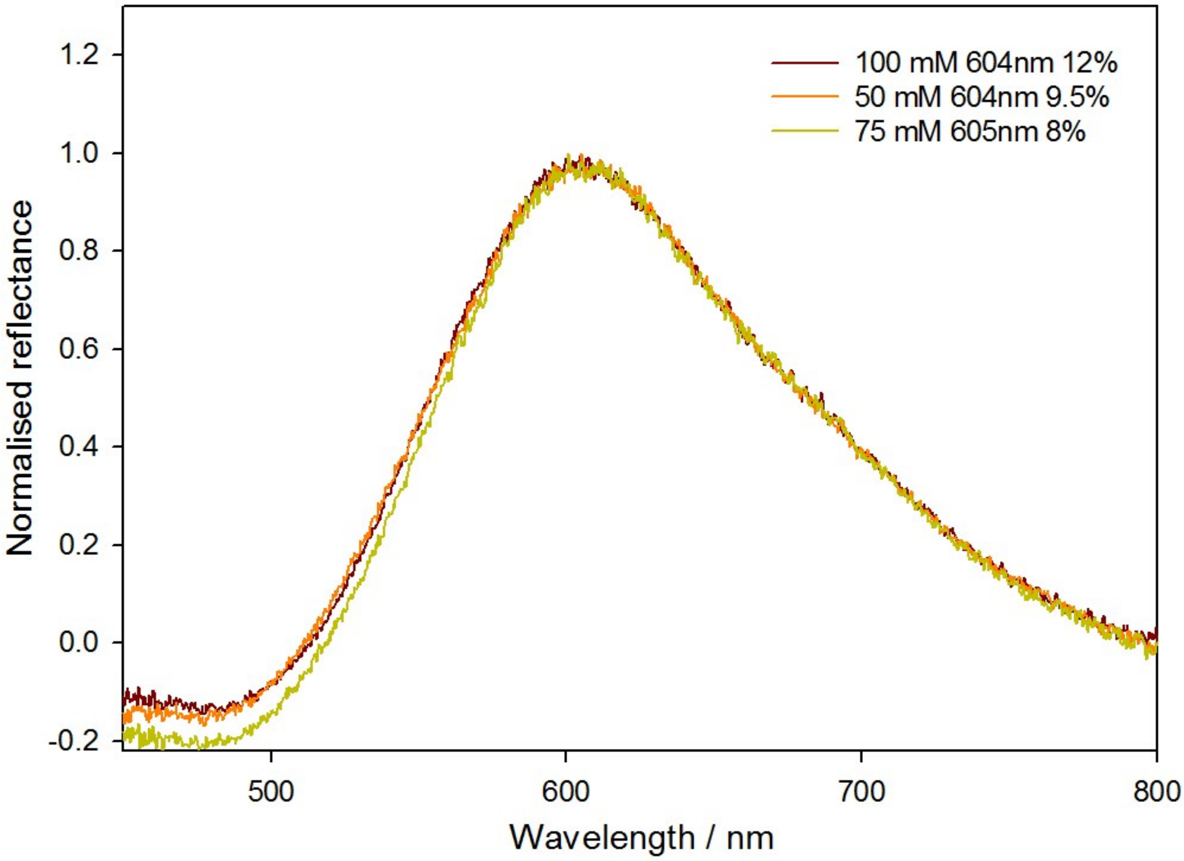
Optical reflectance



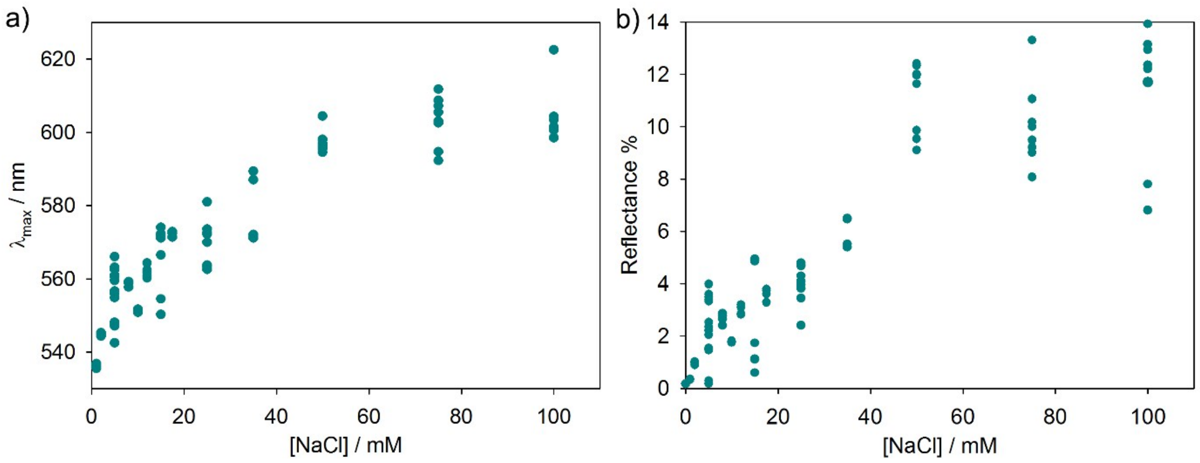
SI Figure 4 Wavelength maxima position from transmission experiments plotted against the wavelength maxima position obtained from reflectance measurements on various NP films assembled at the water-DCE interface. Each measurement was made on the same sample for direct comparison.



SI Figure 5 Plot of reflection maxima position against the corresponding reflectance values.



SI Figure 6 Normalised overlay of three samples yielding similar positions of the reflectance maxima (~ 604 nm) but differing reflectance intensity (12, 8 and 9.5 % for 100, 75 and 50 mM NaCl respectively).



SI Figure 7 Plots of wavelength maxima position (a) and reflectance values (b) for NP layers assembled at a range of NaCl concentrations displaying the spread in data observed for multiple repetitions.

Data for theoretical calculation of optical reflectance

As reported in the main text, NP diameter data measured from X-ray experiments has a mean of 12.74 nm and standard deviation of 0.31 nm. However, based on TEM data the mean and standard deviation of the NP diameter is found to be 12.82 nm and 0.878 nm, respectively. Based on these two sets of experimental data we obtain an estimate for the data to be used for theoretical calculations.

We estimate the mean NP diameter as an average of the two reported above, *i.e.*, $\mu_R = (12.74 + 12.82)/2 = 12.78$ nm. The percentage error (e) in this calculation is obtained based on $e = \sqrt{e_1^2 + e_2^2}$, where e_1 and e_2 represents the percentage error in X-ray and TEM measurements, respectively. Here, $e_1 = 2.43\%$ and $e_2 = 6.85\%$, which makes $e = 7.27\%$. This allows us to approximate the standard deviation as $\sigma_R = 12.78 \times 7.27\% = 0.929$ nm. Therefore in all our theoretical calculations we consider $\mu_R = 12.78$ nm and $\sigma_R = 0.929$ nm.

For mean and standard variation of lattice constant a, we estimate μ_a and σ_a based on the following strategy. Mean values in 'NP centre to centre /nm' columns of Table 1 (NaCl) and Table 2 (TBA TPB) (main text) reported for different concentrations of the corresponding electrolytes are used as μ_a. However, for correctly estimating the error associated with these values we considered σ_a to be the one greater of the two errors: i) the error reported in fitting the 'NP centre to centre /nm' data listed in Table 1 and 2 (main text) or ii) the error calculated as $e\%$ of μ_a. To make it vivid, below we explicitly provide the tables that contain μ_a and σ_a at each concentration level of NaCl (SI Table 3) and TBA TPB (SI Table 4) electrolytes.

SI Table 3 Parameters used for theoretical calculations for different NaCl concentrations

[NaCl]/mM	NP centre to centre (C2C) /nm	μ_a /nm	Error from NP C2C measurement /nm	Error calculated as $e\%$ of μ_a	σ_a /nm
2	36.84 ± 2.61	36.84	2.61	2.68	2.68
5	31.49 ± 1.71	31.49	1.71	2.29	2.29
8	29.91 ± 0.86	29.91	0.86	2.17	2.17
10	28.77 ± 0.40	28.77	0.40	2.09	2.09
12	22.57 ± 1.37	22.57	1.37	1.64	1.64
17.5	22.37 ± 0.71	22.37	0.71	1.63	1.63
25	22.56 ± 0.24	22.56	0.24	1.64	1.64
35	19.16 ± 0.14	19.16	0.14	1.39	1.39
50	17.91 ± 0.31	17.91	0.31	1.30	1.30
75	17.74 ± 0.18	17.74	0.18	1.29	1.29
100	17.35 ± 0.29	17.35	0.29	1.26	1.26

SI Table 4 Parameters used for theoretical calculations for different TBA TPB concentrations

[NaCl]/mM	NP centre to centre (C2C) /nm	μ_a /nm	Error from NP C2C measurement /nm	Error calculated as $e\%$ of μ_a	σ_a /nm
1	50.70 ± 19.0	50.70	19	3.69	19
2	27.80 ± 5.9	27.80	5.9	2.02	5.9
4	19.41 ± 0.54	19.41	0.54	1.41	1.41
8	18.21 ± 0.16	18.21	0.16	1.32	1.32
10	18.59 ± 0.66	18.59	0.66	1.35	1.35

Drude–Lorentz model for permittivity of gold

At optical wavelengths, the dielectric response of a metal is dominated by inter-band transitions that demands extension of the Drude (D) permittivity model to a Drude–Lorentz (DL) one, which is of the following form:

$$\varepsilon_{\mathrm{DL}}(\omega) = \varepsilon_\infty - \frac{\omega_{\mathrm{p,D}}^2}{\omega^2 + i\gamma_{\mathrm{D}}\omega} - \frac{s_1\omega_{\mathrm{p1,L}}^2}{(\omega^2 - \omega_{\mathrm{p1,L}}^2) + i\gamma_{1,\mathrm{L}}\omega} - \frac{s_2\omega_{\mathrm{p2,L}}^2}{(\omega^2 - \omega_{\mathrm{p2,L}}^2) + i\gamma_{2,\mathrm{L}}\omega},$$

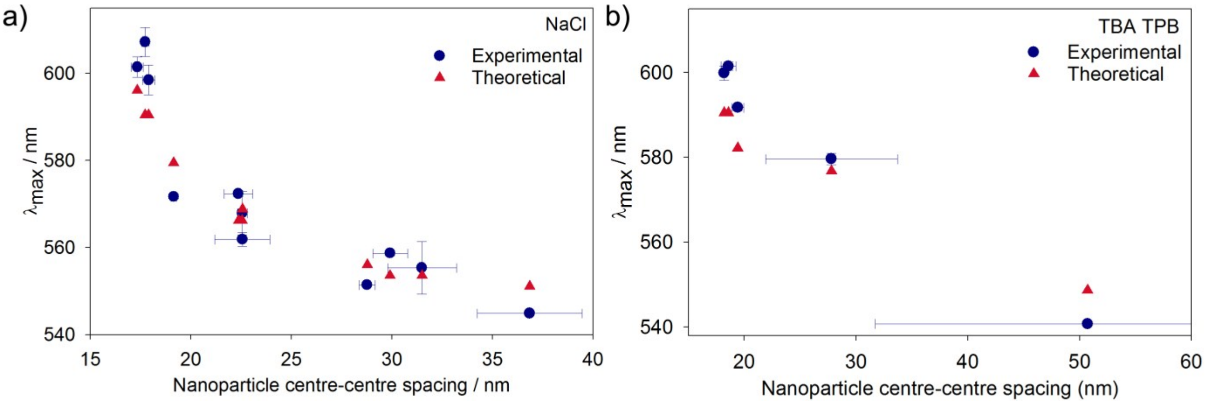
where ε_∞ is the permittivity limit at high frequencies, $\omega_{\mathrm{p,D}}$ and γ_D are the plasma frequency and damping coefficient from the Drude model, respectively. The third and the fourth term are the two additional Lorentzian (L) terms comprising $\omega_{\mathrm{p1,L}}$ and $\omega_{\mathrm{p2,L}}$ as corrections to the plasma frequency (with oscillator strengths of $\gamma_{1,\mathrm{L}}$ and $\gamma_{2,\mathrm{L}}$, respectively, representing the spectral widths of the Lorentz oscillators), besides s_1 and s_2 being the weighting factors.

Here we modelled the permittivity of gold using the parameters listed below which are chosen to closely fit the experimental data [2].

$\varepsilon_\infty = 5.9752$, $\omega_{\mathrm{p,D}} = 8.8667\,\mathrm{eV}$, $\gamma_D = 0.03799$ eV, $s_1 = 1.76$, $\omega_{\mathrm{p1,L}} = 3.6\,\mathrm{eV}$, $\gamma_{1,\mathrm{L}} = 1.3\,\mathrm{eV}$, $s_1 = 0.952$, $\omega_{\mathrm{p2,L}} = 2.8\,\mathrm{eV}$, $\gamma_{2,\mathrm{L}} = 0.737\,\mathrm{eV}$.

As the NPs in this study have diameters ($2R$) much lesser than the mean free path of electrons in gold (which is around 42 nm), we have incorporated size-dependent enhanced scattering losses of surface electrons in the above Drude–Lorentz permittivity model. This effect is incorporated in the permittivity equation in the form of a modified damping coefficient, where γ_D gets replaced by $\gamma_{\mathrm{D}} + \frac{Av_{\mathrm{F}}}{L_{\mathrm{eff}}}$ with v_{F} being the Fermi velocity of electrons in gold, L_{eff} being the reduced mean free path of electrons. The latter can be estimated as $L_{\mathrm{eff}} = \frac{4V}{S}$, where V is the volume and S is the surface area of NPs; (this ratio is $0.75R$ for a nanosphere) [3]. Parameter A is considered to be 0.05 to fit the experimental data.

Combined X-ray diffraction and optical reflectance results



SI Figure 8 Wavelength maxima position of NP layers assembled with NaCl in the aqueous phase (a) and TBA TPB in the organic phase (b) as a function of NP centre to centre spacing.

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