

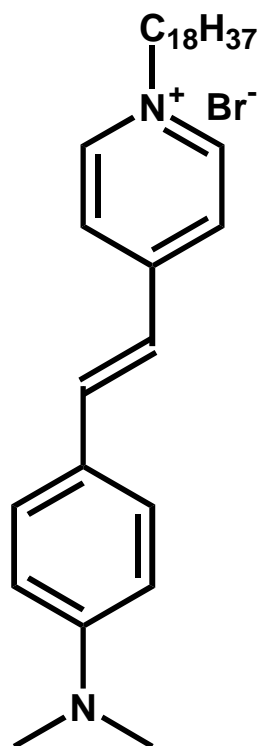
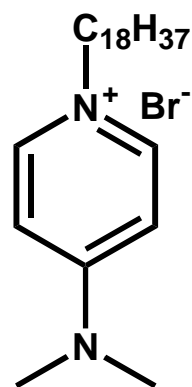
Supporting Information

**Nanoparticle Assembly Following Langmuir-Hinshelwood Kinetics on a
Langmuir Film and Chain Networks Captured in LB Films**

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Contents

	<i>Page No.</i>
Structure of the amphiphiles used in the present study	S2
Pressure-area isotherm and area-time creep plot of ODEP ⁺ Br ⁻ Langmuir films on different subphases	S3
Silver nanoparticles + ODEP ⁺ Br ⁻	S4
Gold nanoparticles + ODP ⁺ Br ⁻	S6
Analysis of the temporal evolution of the extinction spectra of the gold nanoparticle solution and determination of the rate of assembly	S7
Analysis of the subphase in the experiment with gold nanoparticles + ODEP ⁺ Br ⁻	S8
Rate of assembly in the presence of excess citrate	S9
References	S10

Amphiphiles used in the present study**ODEP⁺ Br⁻****ODP⁺ Br⁻**

π -A isotherm and area-time creep plot of ODEP⁺Br⁻ Langmuir films on different subphases

Subphases: water and gold nanoparticle solution

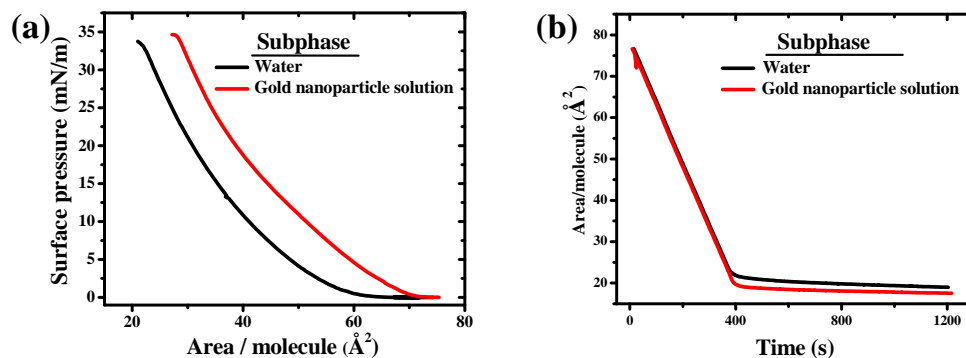


Figure S1. (a) π -A isotherm and (b) area-time plot (at 30 mN/m) of ODEP⁺Br⁻ Langmuir film on water and gold nanoparticle solution as subphase.

On changing the subphase from pure water to gold nanoparticle solution (0.010 mM), the ODEP⁺Br⁻ Langmuir film shows an increase in the area/molecule. Stability of the film with the gold nanoparticle solution subphase is higher, as shown by the decrease in the absolute value of the slope of the area-time creep plot after equilibration at the target pressure ($t \sim 500 - 1200$ s), from 0.002 to 0.001.

Subphases: water and sodium citrate solution

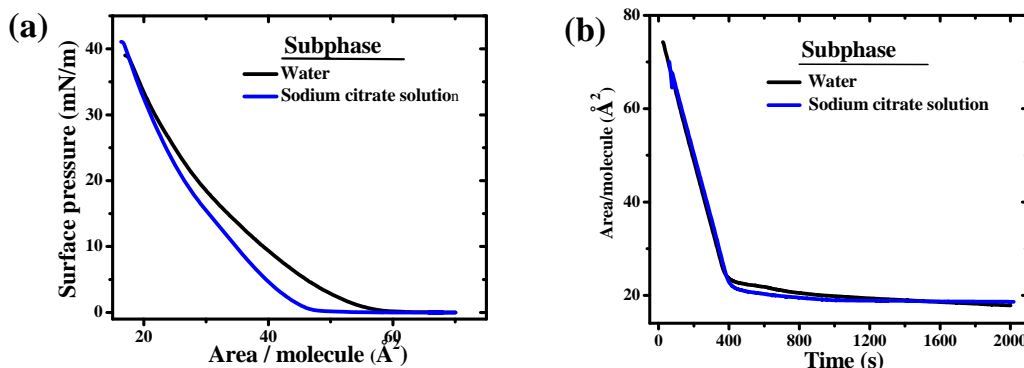


Figure S2. (a) π -A isotherm and (b) area-time plot (at 30 mN/m) of ODEP⁺Br⁻ Langmuir film on water and sodium citrate solution as subphase.

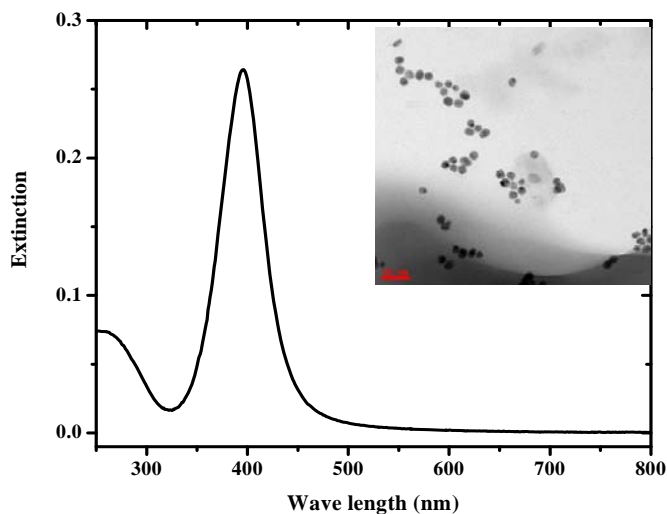
Changing the subphase from pure water to sodium citrate solution (0.01 mM), increases the stability of the ODEP⁺Br⁻ Langmuir film significantly, as shown by the decrease in the absolute value of the slope of the area-time creep plot after equilibration at the target pressure ($t \sim 900 - 2000$ s), from 0.002 to 0.0003.

Silver nanoparticles + ODEP⁺Br⁻

Ag nanoparticles

Silver nanoparticles were prepared by treating silver nitrate with sodium citrate in a water-glycerol medium following reported procedure.^{RI} The LSPR extinction spectrum with the peak at ~ 400 nm and the TEM image of the particles showing size in the range of 12–15 nm are provided in Fig. S3.

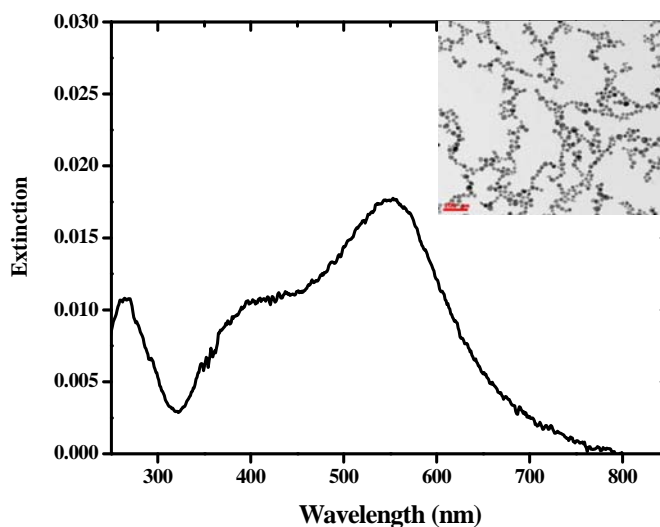
Figure S3. Extinction spectrum of silver nanoparticle solution; the inset shows the TEM image of the nanoparticles (scale bar = 50 nm).



LB film

LB experiment was carried out with the silver nanoparticle solution as the subphase and ODEP⁺Br⁻ monolayer at the air-water interface. The film was transferred to a hydrophilic quartz substrate and a carbon coated copper grid for recording the extinction spectrum and TEM image respectively. In addition to the extinction due to the isolated Ag nanoparticles with $\lambda_{\text{max}} \sim 400$ nm, the LB film shows an extinction with $\lambda_{\text{max}} \sim 550$ nm; the latter corresponds to nanoparticle assemblies as revealed by the network structures observed in the TEM image (Fig. S4).

Figure S4. Extinction spectrum of the LB film of ODEP⁺Br⁻ with silver nanoparticles; the inset shows the TEM image of the film (scale bar = 100 nm).

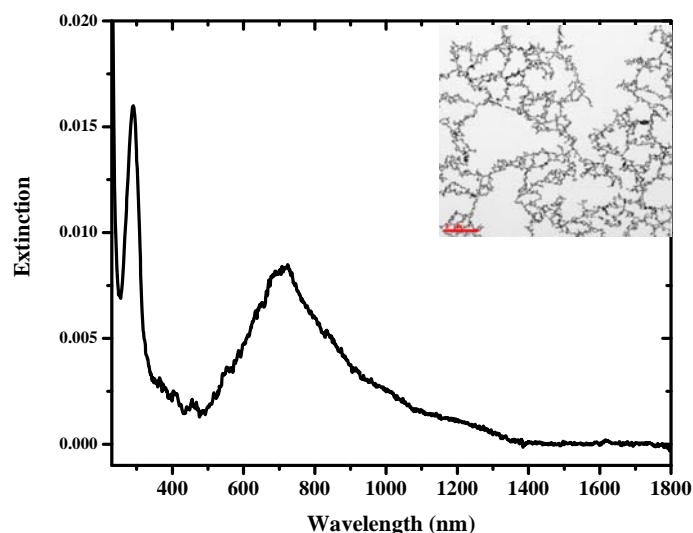


Gold nanoparticles + ODP⁺Br⁻

LB film

LB experiment was carried out with gold nanoparticle solution as the subphase and ODP⁺Br⁻ (Ref. R2) monolayer at the air-water interface. The film was transferred to a hydrophilic quartz substrate and a carbon coated copper grid for recording the extinction spectrum and TEM image respectively. The extinction with $\lambda_{\text{max}} \sim 650$ nm corresponds to gold nanoparticle assemblies as revealed by the network structures seen in the TEM image (Fig. S6).

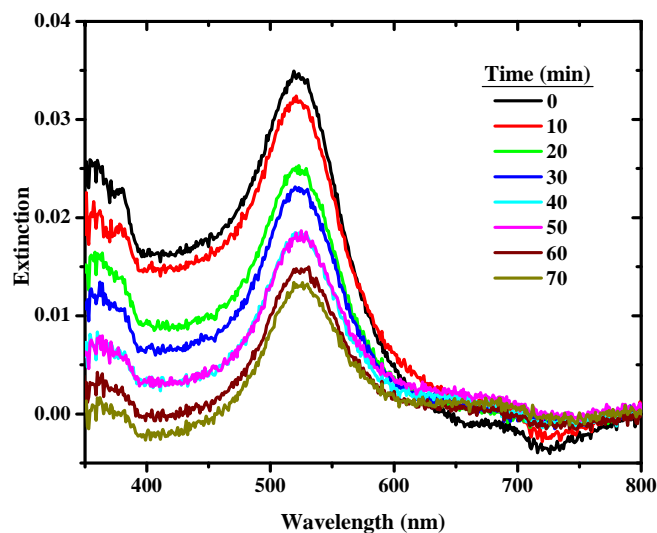
Figure S6. Extinction spectrum of the LB film of ODP⁺Br⁻ with gold nanoparticles; the inset shows the TEM image of the film (scale bar = 1 μm).



Monitoring the assembly process using the nanoparticle solution subphase

150 ml of a 0.011 mM solution of gold nanoparticles was used as the subphase in experiments conducted in a petri-dish. 90 μl of a 1.04 mM chloroform solution of ODP⁺Br⁻ was spread on the nanoparticle solution surface and the extinction spectrum recorded for the 3 ml samples collected every 10 min (Fig. S7). The peak due to the isolated nanoparticles is found to decrease steadily and a peak corresponding to nanoparticle assemblies to emerge concomitantly.

Figure S7. Temporal evolution of the extinction spectra of the gold nanoparticle solution with an ODP⁺Br⁻ monolayer at the air-solution interface.



Analysis of the temporal evolution of the extinction spectra of the gold nanoparticle solution and determination of the rate of assembly

Mie scattering is the main mechanism of scattering when particle size, r and wavelength of light, λ are such that $2\pi r \sim \lambda$. In such a situation, the scattering coefficient, σ scales as $\lambda^{-\alpha}$ where $\alpha = 0.7 - 2.0$.^{R3,R4} The extinction spectra were corrected by estimating the scattering contribution in the full wavelength range, assuming that the intensity at the long wavelength end of 800 nm is primarily due to scattering; a value of 1 was used for α . The spectra were then deconvoluted by nonlinear least square fitting to multiple Gaussians, using MicroCal Origin 7.0, to extract the intensity of the extinction due to the isolated gold nanoparticles. Ratio of the initial concentration to the peak intensity at $t = 0$ min was used to convert the intensity values to concentrations. Plots of the time evolution of the concentration for different initial concentrations are provided in Fig. S8. Slope of the least square fit straight line provides the rates plotted in Fig. 5b in the main text.

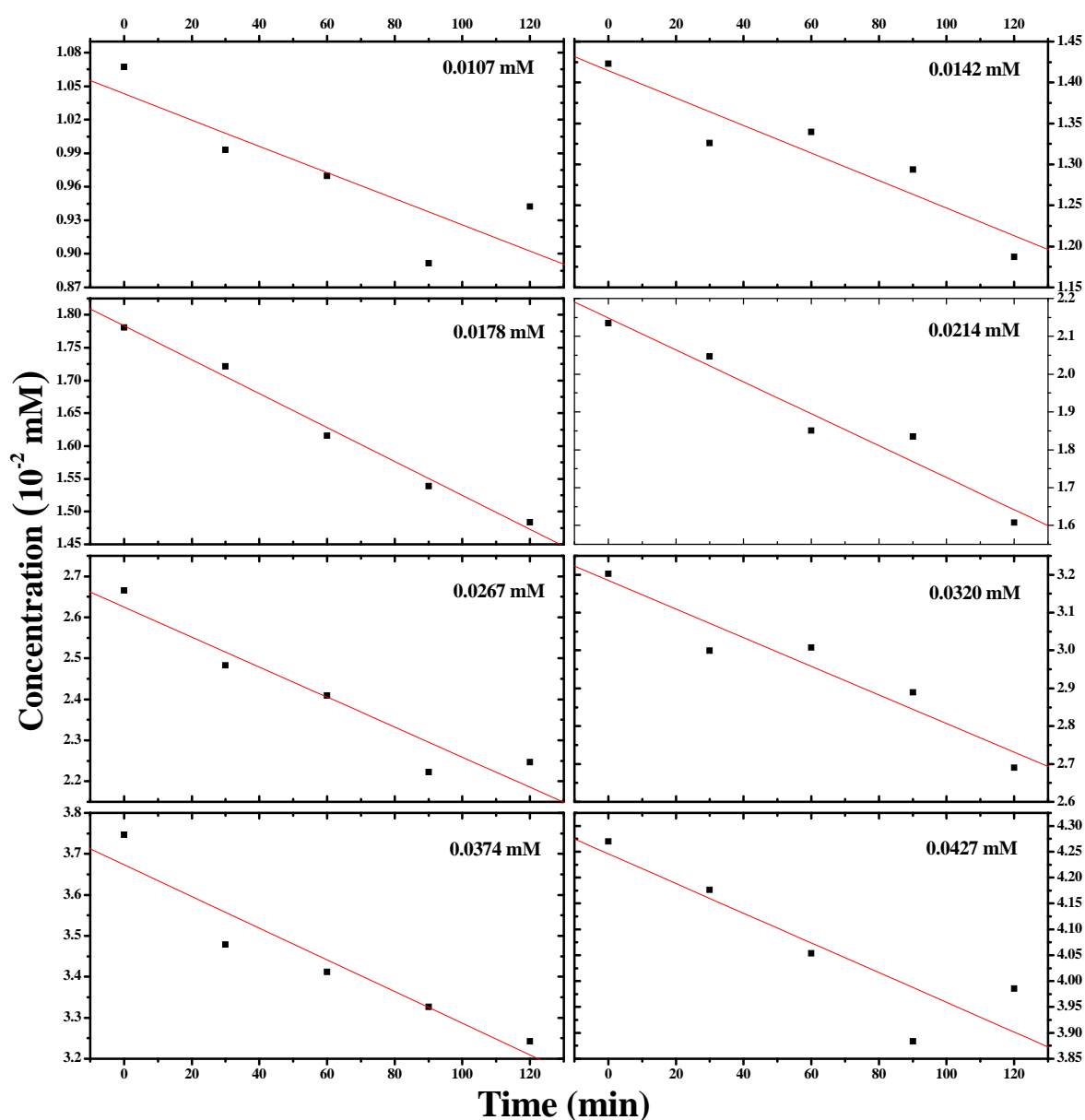


Figure S8. Plot of the concentration of the isolated nanoparticle against time for different initial concentrations of gold nanoparticle solution used as the subphase.

Analysis of the subphase in the experiment on gold nanoparticle + ODEP⁺Br⁻

In the experiment on gold nanoparticle solution taken in a petri-dish with ODEP⁺Br⁻ monolayer spread on the surface, the extinction spectra of the subphase solution exhibited strong scattering effects at long time scales. The scattering is found to increase and then decrease with increasing initial concentration of the nanoparticle solution (Fig. S9). This is consistent with the variation of the rates of assembly shown in Fig. 5b of the main text. TEM images of the samples obtained by evaporating a drop of the solution (Fig. S10) also indicate that the extent of aggregation is highest in the case corresponding to the intermediate initial concentration.

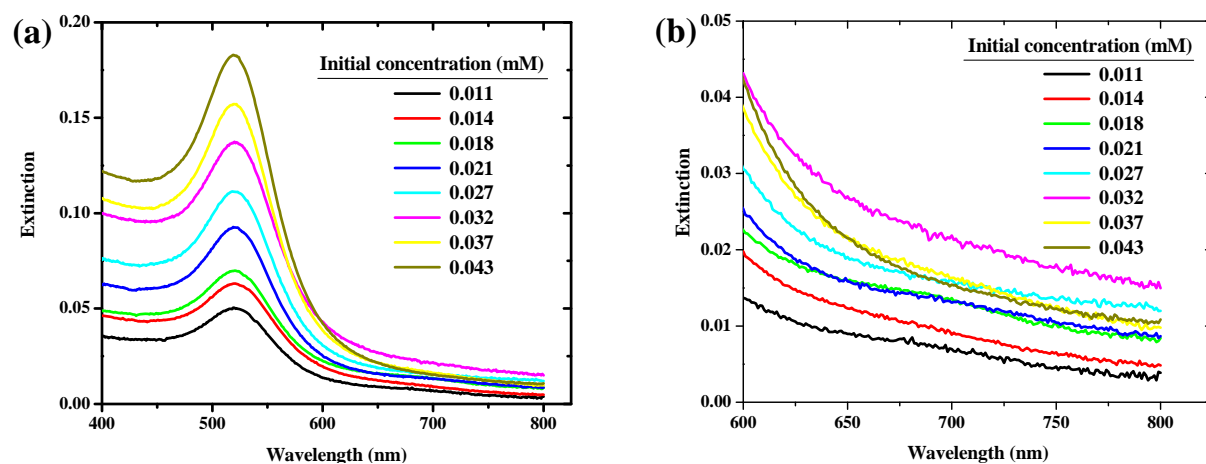


Figure S9.(a) Extinction spectra of the gold nanoparticle solution with different initial concentrations, recorded at 120 min after spreading the amphiphile (ODEP⁺Br⁻) molecules on the surface. Variation of the baseline as a result of the different extents of scattering is highlighted in (b).

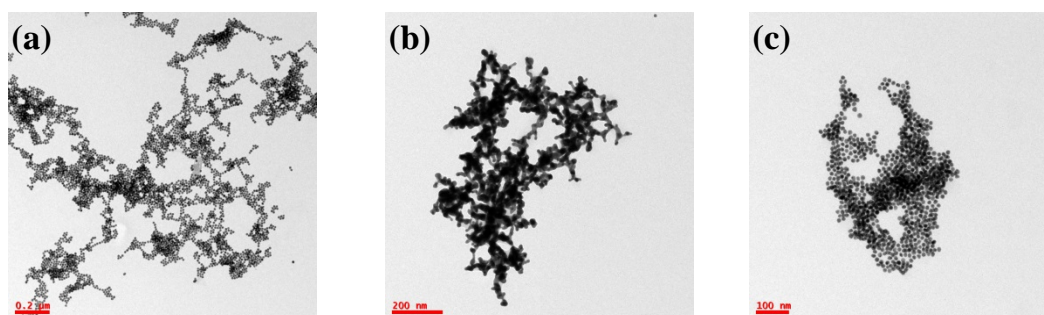


Figure S10. TEM images of samples obtained by drying a drop of the subphase solution with different initial concentrations: (a) 0.011 mM, (b) 0.021 mM and (c) 0.043 mM, collected at 120 min; scale bar = 200 nm (a, b), 100 nm (c).

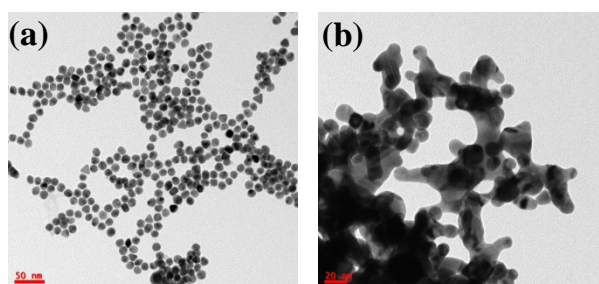
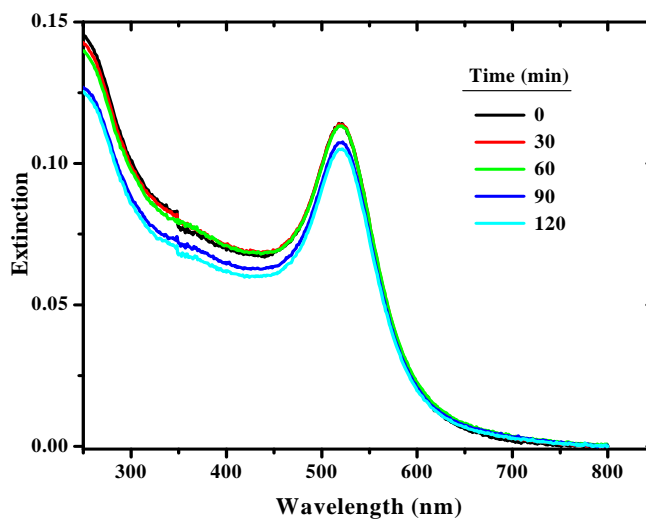


Figure S11. TEM images showing the difference between (a) aggregation and (b) fusing referred to in Fig. 6b of main text.

Rate of assembly in the presence of excess citrate

In order to assess the impact of citrate ions on the adsorption of the gold nanoparticles at the ODEP⁺Br⁻ monolayer at the air-water interface and hence on the rate of their assembly, an experiment was carried out with the initial concentration of 0.021 mM of the gold nanoparticles, but introducing additional citrate ions (equivalent to that which has already been used in the synthesis of the nanoparticles). The temporal evolution of the extinction of the solution shown in Fig. S12 provides a rate of $1.76 \times 10^{-5} \text{ mM min}^{-1}$ which is $\sim 50\%$ lower than the rate observed with the same initial concentration of gold nanoparticles without the additional citrate ions (Figs. 4, 5b in the main text).

Figure S12. Temporal evolution of the extinction spectra of the gold nanoparticle solution (with initial concentration = 0.021 mM and double the amount of citrate compared to the case of similar concentration shown in Fig. 4 of the main text) with an ODEP⁺Br⁻ monolayer at the air-solution interface.



References

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