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Macroscopic and tunable nanoparticle superlattices

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Macroscopic and tunable nanoparticle superlattices

Abstract
We describe a robust method to assemble nanoparticles into highly ordered superlattices by inducing aqueous phase separation of neutral capping polymers. Here we demonstrate the approach with thiolated polyethylene-glycol-functionalized gold nanoparticles (PEG-AuNPs) in the presence of salts (for example, K2CO3) in solutions that spontaneously migrate to the liquid–vapor interface to form a Gibbs monolayer. We show that by increasing salt concentration, PEG-AuNP monolayers transform from two-dimensional (2D) gas-like to liquid-like phase and eventually, beyond a threshold concentration, to a highly ordered hexagonal structure, as characterized by surface sensitive synchrotron X-ray reflectivity and grazing incidence X-ray diffraction. Furthermore, the method allows control of the inplane packing in the crystalline phase by varying the K2CO3 and PEG-AuNPs concentrations and the length of PEG. Using polymer-brush theory, we argue that the assembly and crystallization is driven by the need to reduce surface tension between PEG and the salt solution. Our approach of taking advantage of the phase separation of PEG in salt solutions is general (i.e., can be used with any nanoparticles) leads to high-quality macroscopic and tunable crystals. Finally, we discuss how the method can also be applied to the design of orderly 3D structures.
We describe a robust method to assemble nanoparticles into highly ordered superlattices by inducing aqueous phase separation of neutral capping polymers. Here we demonstrate the approach with thiolated polyethylene-glycol-functionalized gold nanoparticles (PEG-AuNPs) in the presence of salts (for example, K$_2$CO$_3$) in solutions that spontaneously migrate to the liquid-vapor interface to form a Gibbs monolayer. We show that by increasing salt concentration, PEG-AuNP monolayers transform from two-dimensional (2D) gas-like to liquid-like phase and eventually, beyond a threshold concentration, to a highly ordered hexagonal structure, as characterized by surface sensitive synchrotron X-ray reflectivity and grazing incidence X-ray diffraction. Furthermore, the method allows control of the in-plane packing in the crystalline phase by varying the K$_2$CO$_3$ and PEG-AuNP concentrations and the length of PEG. Using polymer-brush theory, we argue that the assembly and crystallization is driven by the need to reduce surface tension between PEG and the salt solution. Our approach of taking advantage of the phase separation of PEG in salt solutions is general (i.e., can be used with any nanoparticles) leads to high-quality macroscopic and tunable crystals. Finally, we discuss how the method can also be applied to the design of orderly 3D structures.

1 Introduction

Self-assembly of nanoparticles and molecular-scale building blocks into hierarchically designed ordered structures provides a promising route for the production of metamaterials and nanodevices through bottom-up approaches.\textsuperscript{1–6} Particularly, chemically stable gold nanoparticles (AuNPs) that seem to possess desirable optical and electronic properties have been assembled into three dimensional (3D) ordered structures by use of complementary single-stranded DNA or DNA origami with unique programmable features.\textsuperscript{4–8} Concomitantly, two-dimensional (2D) self-assembly of AuNPs at solid- or vapor-liquid interfaces have also been developed,\textsuperscript{9–11} providing valuable understanding of general mechanisms involved in self-assembly that can be readily applied in other dimensions. Employing a self- and guided-assembly approach, it has been shown that capped AuNPs, AgNPs, or magnetite with various surfactants (including thiolated-acyl chains, -PEG, and others) can be manipulated in a Langmuir trough to form ordered 2D domains, which can be transferred to solid support by the Langmuir-Blodgett technique for further applications\textsuperscript{12–21}. Recently, it has been shown that unpaired thiolated ssDNA functionalized AuNPs (ssDNA-AuNPs) self-assemble and crystallize at gas-solution interfaces spontaneously simply by tuning various salts concentrations.\textsuperscript{22–24} These studies established that the complexed ssDNA-AuNP is amphiphilic in character by virtue of the polyelectrolytic nature of DNA that competes with the hydrophobicity that is inadvertently introduced in the thiolating process of DNA.\textsuperscript{24} Another approach to 2D assembly exploits electrostatic interactions between a positively charged template formed by a Langmuir monolayer with desired charged headgroups lipids and the negatively charged ssDNA-AuNPs or even unfunctionalized (bare) AuNPs.\textsuperscript{25–27} These studies point to the possibility that the functionalizing DNA can be replaced by macromolecules that display intrinsic amphiphilic character. Thus, inspired by our findings,\textsuperscript{24} we have embarked on a robust approach to explore the interfacial and 3D self-assembly of gold nanoparticles by functionalizing them with polyelectrolytes and amphiphilic polymers. Here, we report on the properties and self-assembly of polyethylene-glycol (PEG)-functionalized AuNPs (PEG-AuNPs). PEG is a remarkable linear polymer that resides on the hydrophobic/hydrophilic edge where one or the other (hydrophobic or hydrophilic) can be readily tweaked by varying salts
concentrations, pH, and temperature.\textsuperscript{28,29} These properties of PEG mixed with dextran or salts have been widely used in the separation and extraction of macromolecules and organelles of cells by the so called aqueous biphasic systems technique (ABS).\textsuperscript{30–32} Owing to PEG’s biocompatibility and the low cytotoxicity of Au, studies of PEG-AuNPs have been focused towards nanomedicine applications.\textsuperscript{33–35} Grazing incidence small-angle X-ray scattering (GISAXS) and X-ray reflectivity (XRR) are used to determine the in-plane structure and surface-normal density profile, respectively, of self-assembled PEG-AuNPs at the vapor-liquid interface by manipulating the concentration of a specific salt, K$_2$CO$_3$ that has been efficiently used in ABS.\textsuperscript{30,31} The evolution of 2D PEG-AuNP superlattice formation is systematically studied with two kinds of PEG (molecular weight of 6000 and 800) by manipulating K$_2$CO$_3$ and PEG-AuNP concentrations.

2 Experimental

2.1 Reagents and Materials

Poly(ethylene glycol) methyl ether thiol (PEG-SH; Sigma-Aldrich) with average molecular weight of 800 and 6000 g/mol (the number of monomer $N = 18$ and 136, respectively; Kuhn length $b = 7.24$ Å; See the Supplementary Information) was dissolved in degassed Millipore water with slight sonication. The freshly-prepared PEG-SH solution was added to aqueous suspension of AuNPs, with nominal size of 10 nm (Ted Pella) in large excess (molar ratio of PEG-SH/AuNP $\approx 6000$) under vigorous stirring. The mixture of PEG-SH and AuNPs was gently stirred at room temperature for one day to allow for maximum PEG loading after ligand exchange. The as-prepared PEG-AuNPs were concentrated via centrifugation (at 20000g $\times$ 1h). The supernatant was discarded and the precipitate was collected and redispersed in Millipore water. This washing process with centrifugation and redispersion was done at least twice prior to further measurements. The concentration of PEG-AuNPs was determined by UV-Visible absorption measurements. Aqueous solution of potassium carbonate (anhydrous, K$_2$CO$_3$; Fisher Scientific) was prepared and mixed with PEG-AuNPs suspensions at desired concentrations of K$_2$CO$_3$ (0.05–1000 mM) and PEG-AuNPs (0.05–10 nM) prior to X-ray measurements. We note that PEG-AuNPs form visible precipitates at 1 M K$_2$CO$_3$ after overnight incubation, while they are stable as suspension for months at low K$_2$CO$_3$ concentrations.

2.2 Experimental Setup

Specular X-ray reflectivity (XRR) and grazing incidence small-angle X-ray scattering (GISAXS) measurements were conducted on the liquid surface spectrometer (LSS) at beamline 9ID-B, Advanced Photon Source (APS), Argonne National Laboratory. The aqueous solution of the PEG-AuNPs in absence and presence of K$_2$CO$_3$ was contained in a shallow trough (surface area 6 × 6 cm$^2$ and enclosed in gas tight canister) where the aqueous surface was illuminated with a highly collimated and monochromatic X-ray beam (photon energy $E = 8.0$ keV and wavelength $\lambda = 1.5497$ Å). For an XRR measurement, a point detector (Bicron) that moves within the scattering plane, was used to collect the X-ray reflectivity from the surface at the exit angle (with respect to the surface) $\alpha$ in such way that $\alpha = \alpha_x, \alpha_y$ being the X-ray incident angle with respect to the surface. The reflectivity, $R$, was measured as a function of $Q$, that equals $(4\pi/\lambda)\sin\alpha$ and is the z-component (along the surface normal) of the moment transfer $Q$. The trough was allowed to move laterally to provide fresh portions of the surface in the course of the reflectivity measurement. For a GISAXS measurement, a digital, two-dimensional Pilatus 100K detector (487 × 195 pixels, 172 × 172 μm per pixel) was placed downstream from the sample and was calibrated with the standard calibrating material, i.e., silver behenate powder. The GISAXS intensity was obtained as a function of the three orthogonal components denoted as $(Q_x, Q_y, Q_z)$, where $Q_x$ component is along the surface normal, while $Q_y$ and $Q_z$ components are parallel to the surface. In this study, $Q_y$ is defined as parallel to the detector surface while $Q_z \approx 0$. Thus, the magnitude of the in-plane scattering vector, $Q_{xy}$, defined as $\sqrt{Q_x^2 + Q_y^2}$, is practically equivalent to $Q_y$. In the small angle regime, $Q_y \approx (4\pi/\lambda)\theta$, 2θ being the in-plane scattering angle. The X-ray exposure time and incident beam attenuation were carefully chosen in such way that each GISAXS frame has a good signal to noise ratio and sample radiation damage was minimized. The trough was sealed in a canister that has Kapton windows for X-ray passage. It was purged with water-saturated helium in the course of the X-ray measurements to minimize the background scattering and radiation damage. The instrumental details can be found elsewhere.\textsuperscript{36} Solution small-angle X-ray scattering (SAXS) experiments for determining the size of the nanoparticles in suspension were performed on beamline 12ID-B at APS with similar setups employed for biomolecules before.\textsuperscript{27,37}

3 Results and Discussion

GISAXS patterns as functions of $Q_{xy}$ and $Q_z$ for aqueous solutions of PEG$_{6k}$-AuNPs without salts and with 500 mM K$_2$CO$_3$ are shown in Fig. 1a. In the absence of salts, sector-shaped and broad circular features at low and high $Q_{xy}$ ranges originate from the form factor of PEG$_{6k}$-AuNPs, which is dominated by the bare form factor of AuNPs (see SI).\textsuperscript{24,27} This indicates that PEG$_{6k}$-AuNPs spontaneously accumulate at the interface without any salts in solutions albeit dispersed at low coverage. As shown in Fig. S1, the corresponding GISAXS pattern of unfunctionalized (bare) AuNPs without PEG does not show any features associated with the form factor. Although GISAXS patterns from aqueous solutions of pure PEG$_{6k}$ without or with salts do not show any features different from water surface in the current $Q_{xy}$ window (Fig. S1), PEG itself has been reported to form Gibbs monolayers at the air-water interface.\textsuperscript{28,29,38–40} Clearly, PEG drives the functionalized PEG$_{6k}$-AuNPs to the gas-water interface. However, as the GISAXS pattern shows, the particles are not correlated. By contrast, in the presence of 500 mM K$_2$CO$_3$, up to 5 sharp Bragg rods become apparent, evidencing the formation of a long-range ordered crystalline layer of PEG$_{6k}$-AuNPs at the interface. Figure 1b shows horizontal linecut profiles along $Q_{xy}$ direction (at $Q_z = 0.020$ Å$^{-1}$) from the GISAXS patterns in Fig. 1a. The linecut profile from PEG$_{6k}$-AuNPs mixed with 500 mM K$_2$CO$_3$ represents a combination of both form factor (See SAXS data from bulk solution...
in Fig. S2) and structure factor.\textsuperscript{24,27} The extracted structure factor at the low $Q_z$ range (0.02–0.1 Å\textsuperscript{-1}) is plotted in Fig. 1c. The diffraction peak-positions ratios with respect to the fundamental peak ($Q_2 = 0.0225$ Å\textsuperscript{-1}) satisfy $Q_i / Q_1 \approx 1 : \sqrt{3} : \sqrt{4} : \sqrt{7} : \sqrt{9} : \ldots$ ($i = 1–9$) revealing the formation of a long-range ordered 2D hexagonal superlattice of AuNPs with an inter-particle distance of $a_L = 4\pi / (\sqrt{3} Q_1) = 322$ Å, where the corresponding diffraction peaks are indexed as (10), (11), (20), (21), (30) and higher-order Bragg reflections. This demonstrates that K$_2$CO$_3$ plays a crucial role in promoting interfacial self-assembly and crystallization of PEG$_8$AuNPs. Recently, single-stranded DNA functionalized AuNPs (ssDNA-AuNPs) have been found to form a Gibbs monolayer and crystallize as hexagonal superlattices at the vapor-liquid interface.\textsuperscript{22–24} Here, the PEG$_8$AuNP/K$_2$CO$_3$ exhibits much higher crystalline quality exemplified by nine Bragg reflections. Below, we describe the evolution of PEG$_8$AuNP superlattices systematically by regulating K$_2$CO$_3$ or PEG-AuNP concentrations.

The GISAXS patterns in Fig. 2a for aqueous solutions of 5 nM PEG$_8$AuNPs mixed in varying amounts of K$_2$CO$_3$ in the range of 0.05 – 1 M indicate an in-plane structural transformations from uncorrelated to short-range ordering, and eventually to long-range hexagonal order at threshold concentration of about 5 mM K$_2$CO$_3$. Furthermore, the linecut profiles in Fig. 2b show that the hexagonal inter-particle distance decreases with the increase of salt concentration, as evidenced by gradual peaks-positions shift to higher $Q_{xy}$ values. This demonstrates that K$_2$CO$_3$ is capable of tuning the 2D hexagonal superlattice at the vapor-liquid interface such that the lattice constant $a_L$ takes values in the range $a_L = 245 – 388$ Å under the current tested conditions (see more details in Table 1). For concentrations 5 – 500 mM K$_2$CO$_3$, the diffraction peaks are extremely sharp with a peak full-width-at-half maximum (FWHM) of the (10) reflection (FWHM$_{(10)} \approx 0.0003 – 0.0006$ Å\textsuperscript{-1}) that is comparable to the instrumental resolution ($\approx 0.0003$ Å\textsuperscript{-1}), suggesting that the estimated crystalline size is on the micrometer scale, significantly larger than that found in 2D superlattices formed by ssDNA-AuNPs.\textsuperscript{22,24} At the highest K$_2$CO$_3$ concentration (1 M) the FWHM$_{(10)} \approx 0.0019$ Å\textsuperscript{-1} with a 2D crystalline size on the order of 3.4 × 10\textsuperscript{3} Å, which is still superior than that found in ssDNA-AuNPs superlattices.\textsuperscript{22,24} This trend suggests that higher K$_2$CO$_3$ concentrations, while promoting the formation of denser packing of AuNPs, induce defects in the superlattices and tend to decrease the crystalline size (Table 1).

In addition to its dependence on K$_2$CO$_3$ concentration, the self-assembly depends on the PEG$_8$AuNP concentration, as shown in Fig. S3 at a fixed K$_2$CO$_3$ 500 mM at various concentrations of PEG$_8$AuNPs (0.05 – 10 nM). The GISAXS patterns as well as the corresponding linecut profiles in Fig. S3b show that short-range hexagonal order emerges at 0.25 – 0.5 nM PEG$_8$AuNPs, and at higher concentrations long-range order of micrometer size 2D crystallines sets in with $a_L = 338 ± 4$ Å and $a_L = 309 ± 3$ Å at 2.5 and 10 nM, respectively (see Table 1). Qualitatively, the effect of nanoparticle concentration on monolayer density and compressibility can be understood via the Gibbs adsorption. Increasing the nanoparticle concentration in the bulk leads to an increase of nanoparticle surface density and the corresponding increase of surface pressure, originating from the entropy and inter-particle interaction, similar to the soft crystallization of ssDNA-AuNPs.\textsuperscript{6}

AuNPs functionalized with a shorter chain PEG (MW = 800) show similar 2D superlattices under similar conditions to those used for PEG$_8$AuNPs discussed above. GISAXS patterns in Fig. S4 show the evolution of the self-assembly and crystallization of a fixed concentration PEG$_{800}$-AuNPs and varying the amount of K$_2$CO$_3$ in solution, and Fig. S5 shows the development at a fixed 500 mM K$_2$CO$_3$ for various PEG$_{800}$-AuNPs concentrations. Compared to PEG$_8$AuNPs, the diffractions peaks of PEG$_{800}$-AuNPs shift to larger $Q_{xy}$ values, evidence for closer packing as expected for a shorter and smaller dynamical radius of PEG$_{800}$-AuNPs (See Fig. S7). We note that crystallization of PEG$_{800}$-AuNPs is observed only for high concentrations of K$_2$CO$_3$ and PEG-AuNPs, i.e., $a_L = 149 ± 1$ Å at 1 M K$_2$CO$_3$ and 5 nM PEG$_{800}$-AuNPs, and $a_L = 158 ± 1$ Å at 500 mM K$_2$CO$_3$ and 10 nM PEG$_{800}$-AuNPs.

To determine the density profile of the crystalline film across

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.pdf}
\caption{K$_2$CO$_3$ induced 2D superlattices of PEG$_8$-AuNPs at the vapor-liquid interface. (a) GISAXS patterns as functions of $Q_x$, and $Q_z$ for aqueous solutions of 5 mM PEG$_8$-AuNPs in the absence of salts and in the presence of 500 mM K$_2$CO$_3$. Intensities are displayed on logarithmic scales. (b) Horizontal linecut profiles along $Q_x$, direction at $Q_z = 0.020$ Å\textsuperscript{-1} integrated over $Q_y$ range $5 × 10^{-3}$ Å\textsuperscript{-1} in the GISAXS 2D patterns for Gibbs monolayers of PEG$_8$-AuNPs in the absence of salts (circles) and in the presence of 500 mM K$_2$CO$_3$ (squares). Solid lines are guides to the eyes. The arrows point to the calculated positions of higher orders Bragg reflections based on the the fundamental diffraction peak of a 2D hexagonal lattice. The plots are vertically shifted for clarity. (c) The extracted structure factor, $S(Q_{xy})$, profile at low $Q_{xy}$ range (0.02–0.1 Å\textsuperscript{-1}) for the Gibbs monolayer of PEG$_8$-AuNPs mixed with 500 mM K$_2$CO$_3$. The peak positions ratios with respect to the fundamental diffraction peak of 1 : $\sqrt{3}$ : $\sqrt{4}$ : $\sqrt{7}$ : $\sqrt{9}$ : $\ldots$ reveals a hexagonal packing of nanoparticles with corresponding diffraction indices (10), (11), (20), (21), (30) and higher-order Bragg reflections.}
\end{figure}
the interface we employ X-ray reflectivity, which provides the electron density (ED) profile, $\rho$, as function of depth (along $z$-axis, i.e., the surface normal) by refining a model that fits the reflectivity data through the Prarratt’s recursive method.\textsuperscript{36,41,42}

Figure 3 shows X-ray reflectivity normalized to that of ideally flat water, $R/R_F$, for PEG$_{6k}$-AuNPs and PEG$_{800}$-AuNPs at 5 nM in the presence of different amounts of K$_2$CO$_3$ in the aqueous subphase as indicated (these are the same samples on which the GISAXS described above have been performed). The dramatic increase of the first maximum in $R/R_F$ with the concentration of K$_2$CO$_3$, as shown in both (a) and (c) signals a huge accumulation of capped-AuNPs at the interface. Quantitative analysis of the $R/R_F$, based on the effective-density model\textsuperscript{43}, yields the corresponding ED profiles shown in (b) and (d) with an enhancement region over that of the solution on a $\approx$ 100 Å length scale, very close to the diameter of AuNPs ($D = 88 \pm 9$ Å, see Fig. S2). The ED of densely packed PEG as well as water-saturated-PEG is very close to that of the water subphase, therefore yielding only a small increase in the ED of the submerged polymer tails, whereas at the air/particle interface, a $\sim$ 50 Å strata can be associated with densely-packed PEG, as depicted in Fig. 4. This practically indicates that the films that are formed at the surface consist of a mono-particle layer, and combination of the GISAXS and $R/R_F$ results allows determination of surface coverage and conformation of the particles as discussed below. We note that the maximum $R/R_F$ for PEG$_{800}$-AuNPs film are much higher than PEG$_{6k}$-AuNPs under otherwise identical conditions (i.e., concentrations of AuNPs and K$_2$CO$_3$). This higher surface density compared to PEG$_{6k}$-AuNPs is consistent with the corresponding difference in lattice parameters of the two capped-AuNPs. Based on the measured lattice parameters obtained by GISAXS, the ED of a thin slab of 2D crystalline and using a simple space filling model (See details in SI), we estimate the surface coverage of pure 2D hexagonal superlattice is nearly 100%. The observation of limited lattice constant tunability for the shorter PEG indicates that the relatively more rigid PEG$_{800}$-AuNPs remain in the liquid state (short range order) over a wider range of salt concentrations compared to the softer PEG$_{6k}$-AuNPs.

Our main results are summarized in phase-diagrams of PEG-AuNPs versus K$_2$CO$_3$ concentrations as shown in Fig. 5 for both polymers. At low K$_2$CO$_3$ and PEG-AuNPs concentrations, the accumulated particles at the interface lack any order forming a gas-like phase. In the intermediate concentrations of K$_2$CO$_3$ and PEG-AuNPs, more PEG-AuNPs adsorb at the interface and promote formation of liquid-like state of short-range hexagonal order. At threshold concentrations of K$_2$CO$_3$ and PEG-AuNPs, a long-range order phase of 2D hexagonal superlattices is established with total surface coverage (nearly 100%). At concentrations $\geq$ 1 M K$_2$CO$_3$ the PEG-AuNPs precipitate most likely in simple 3D structure (fcc, for instance). The phase diagram of PEG$_{6k}$-AuNPs shows that the lattice constant can be tuned by both K$_2$CO$_3$ and PEG-AuNP concentrations without loss of materials due to pre-

Table 1 Lattice parameters of 2D superlattice of PEG$_{6k}$-AuNPs at the vapor-liquid interface induced by K$_2$CO$_3$

<table>
<thead>
<tr>
<th>[PEG$_{6k}$-AuNPs] (nM)</th>
<th>[K$_2$CO$_3$] (mM)</th>
<th>$Q_1$ (Å$^{-1}$)</th>
<th>Lattice constant, $a_L$ (Å)</th>
<th>FWHM (Å$^{-1}$)</th>
<th>Estimated crystalline size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
<td>0.0187</td>
<td>388 ± 4</td>
<td>~-0.0003</td>
<td>2.1 $\times$ 10$^4$</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>0.0198</td>
<td>366 ± 5</td>
<td>~-0.0004</td>
<td>1.5 $\times$ 10$^4$</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>0.0225</td>
<td>322 ± 3</td>
<td>~-0.0006</td>
<td>1.0 $\times$ 10$^4$</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>0.0296</td>
<td>245 ± 2</td>
<td>~-0.0019</td>
<td>3.4 $\times$ 10$^3$</td>
</tr>
<tr>
<td>2.5</td>
<td>500</td>
<td>0.0215</td>
<td>338 ± 4</td>
<td>~-0.0007</td>
<td>8.4 $\times$ 10$^3$</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>0.0225</td>
<td>322 ± 3</td>
<td>~-0.0006</td>
<td>1.0 $\times$ 10$^4$</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
<td>0.0235</td>
<td>309 ± 3</td>
<td>~-0.0004</td>
<td>1.7 $\times$ 10$^4$</td>
</tr>
</tbody>
</table>

Fig. 2 In-plane structure evolution of 2D superlattices from aqueous solutions of 5 nM PEG$_{6k}$-AuNPs at various K$_2$CO$_3$ concentrations. (a) GISAXS patterns as functions of $Q_1$ and $Q_2$ for aqueous solutions of 5 nM PEG$_{6k}$-AuNPs in the presence of 0.05 to 1 M K$_2$CO$_3$. Intensities are displayed on logarithmic scales. (b) Horizontal linecut profiles along $Q_1$, direction at $Q_2 = 0.020$ Å$^{-1}$ integrated over $Q_1$ range $5 \times 10^{-3}$ Å$^{-1}$ at low $Q_1$ range (0.02–0.07 Å$^{-1}$) for Gibbs monolayers of 5 nM PEG$_{6k}$-AuNPs at various K$_2$CO$_3$ concentrations as indicated. The plots are vertically shifted for clarity.
Based on the reported phase diagrams of PEG-salt solutions, there is a single and a two phase region, consisting of a high salt and a low salt plus PEG phases. Even in the region of the single component phase, our results show finite interfacial accumulation suggesting that there is a depletion of ions within the spherical brush, which induces an osmotic pressure gradient. Nevertheless, we find that the effect of salt (0 to 0.5 M) on the hydrodynamic radius of PEG-AuNPs is negligible (see SI). This observation can be explained by a blob size $\xi$ that is smaller than the thermal correlation length $\xi_t$, thus leading to chains that are ideal and a solvent (water+salt) inside the brush that is at the $\theta$-point. Still, the overall surface tension of the entire brush with the poor solvent (high salt concentration) is very significant (of order 60 – 250$k_B T$ for PEG$_{6k}$-AuNPs), so the PEG-AuNPs readily migrate to the interface, where such surface tension can be drastically reduced. Under this picture, the effective (hydrodynamic) spherical radius of a given PEG-AuNP ($R_h$) with Au-core radius $R$ is given by

$$
(\frac{R_h}{R})^2 = 1 + 2N\frac{b^2\sigma^1/2}{R} (2w_0)^{1/4},
$$

where $N$ is the number of Kuhn monomers, $b$ is the Kuhn length ($b = 7.24$ Å for PEG), $\sigma$ is the grafting density ($\approx$ 1.51 chains/nm$^2$), and $w_0$ is a dimensionless three body interaction, where we use the Flory result $w_0 = 1/6$, so that $(2w_0)^{1/4} = 0.76$. Using the parameters derived in the SI yield $D_h = 2R_h = 35.5$ nm consistent with the measured 39.9(13) nm for PEG$_{6k}$-AuNPs whereas for PEG$_{800}$-AuNPs, $D_h = 15.3$ nm, significantly shorter than the measured 22.3(7) nm. We note that Eq. 1 is valid for an infinite chain and that PEG$_{800}$ consists of only $\approx$ 9 independent (Kuhn-length) segments, suggesting a much more rigid polymer corona. Indeed the phase diagram for PEG$_{800}$-AuNPs shows a very narrow range of crystallinity as the corona around the particle is much less compressible than that of the longer polymer. It is interesting to note that the measured hydrodynamical radius $R_h$ does not shrink with the increase of ionic strength, as is usually observed for polyelectrolytes-brushes or ssDNA-AuNPs, but rather migrate to the interface to maintain minimal chain-contact with the poor solvent and form a densely packed hexagonal lattice - compressible for the long chain PEG and incompressible for the shorter chain. As detailed in the SI and the use of dynamic lattice theory (DLT), the lattice constant at the interface ($a_L$), can be determined by the balance between the surface tension and the compression of the brush, leading to a simplified form that shows the dependence of the lattice constant on PEG-AuNP concentration $n_f$ and the surface tension between PEG and the
Fig. 4 A schematic of 2D self-assembly and crystallization of PEG-AuNPs at liquid-vapor interface induced by K$_2$CO$_3$ (a) side view and (b) top view.

Fig. 5 Phase diagram as functions of concentrations of K$_2$CO$_3$ and total PEG-AuNPs in the system of (a) PEG$_{6k}$-AuNPs, (b) PEG$_{800}$-AuNPs. The presumptive surface density of PEG-AuNPs (number of NPs/surface area) is provided on the right axes. The symbols (circles, triangles and squares) are presented as sample conditions measured by GISAXS and XRR. The Gibbs monolayer consists of 2D gas-like (uncorrelated), 2D liquid (short range ordering, SRO) and 2D superlattice (long range ordering, LRO) phases at various conditions. 2D superlattice phase becomes unstable and form visible precipitates (3D solid) above 1 M K$_2$CO$_3$ as confirmed by SAXS. The crosshatching area below the critical surface density $\Gamma_c$ indicates that the interfaces could not be fully covered by PEG-AuNPs if all the PEG-AuNPs had migrated to the interfaces. The $\Gamma_c$ is calculated as $1/(R_h + \Delta R_h)^2$, where $R_h$ and $\Delta R_h$ are the mean and spread of hydrodynamic radii of PEG-AuNPs, respectively. Note: The phase boundaries are by no means exact and they are surmised based on the limited datasets.
In a salt free solution, the long chain PEG$_{6k}$ corona is consistent with an infinitely long brush in $\theta$-solvent. However, we find that the hydrodynamic radius of the PEG-AuNPs is practically independent of salt concentration (up to 0.5 M). Heuristically, this can be explained in terms of an effective semipermeable membrane surrounding the corona that maintains a constant salt concentration up to the $\theta$-point. Effectively, the PEG-AuNPs reside in a low salt concentration (liquid A) that is separated at the boundaries of the corona from high concentration salt (liquid B) with an effective surface tension $\gamma_B$ between the two liquids. Even though the surface tension energy per polymer is low (less than $k_BT$), thus preventing the polymer from shrinking, the overall surface tension for the entire PEG-AuNP is very large (of order of 100$k_BT$ or more for the PEG$_{6k}$-AuNPs) and drives the self-assembly and, through optimization of the packing of PEG chains, to crystallization. The tunability of the 2D hexagonal superlattice structure can be achieved over a very wide range by manipulating salt or PEG-AuNPs concentrations and also by the choice of polymer length. Here, we also provide a method to engineer 3D crystals, since sufficiently high salt or PEG-AuNP concentrations induce the formation of 3D precipitates (see Fig. 5), which will be further explored and optimized in the future.

5 Acknowledgments

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References

Control experiments

Figure S1 (a-d) shows a few GISAXS patterns from various solutions as control experiments to demonstrate the importance of functionalizing the AuNPs with PEG and the effect of salt on the formation of superlattice structures. None of the patterns indicate surface enrichment.

Figure S2 shows SAXS measurements of PEG-AuNPs and unfunctionalized (bare) AuNPs dispersed in solution (conducted at Sector 12ID-B at the Advanced Photon Source). The analysis of the measured form factors determines the size and size-distribution of the nanoparticles.
AuNPs. These results demonstrate that the form factor is dominated by Au cores regardless of functionalization as the corona formed by PEG around the AuNP has practically the same electron density as that of the water solution (the SAXS data in Fig. S2 are obtained after subtraction of the SAXS of the solvent). This is crucial to the analysis of the X-ray reflectivity analysis given in the main manuscript that shows the ED of the film is dominated by the AuNPs and the submerged corona is practically indistinguishable from the solution.

**Superlattice dependence on PEG$_{6k}$-AuNPs concentrations**

In the main manuscript we show the tunability of the hexagonal superlattice by varying salt concentration. Figure S3 shows the GISAXS patterns from various concentrations of PEG$_{6k}$-AuNPs at a fixed 0.5 M of K$_2$CO$_3$. Our theoretical model shows a dependence of the lattice constant that is logarithmic in the AuNPs concentration.

![GISAXS patterns](image)

**Short chain PEG$_{800}$-AuNPs crystallization**

In this Section, we present the evolution of the Gibbs monolayer from the gas- to liquid- to superlattice-crystallization of PEG$_{800}$-AuNPs both as a function of salt concentration, Fig. S4 and as a function of PEG-AuNP concentration, Fig. S5. The analysis shows that the crystallization takes place only at much higher K$_2$CO$_3$ concentrations than for PEG$_{6k}$-AuNPs and as expected the lattice constant scales with the length of PEG, thus the length of PEG can be used as a knob to tune the lattice constant as well.

![GISAXS patterns](image)
Fig. S5 (a) GISAXS patterns as functions of $Q_{xy}$ and $Q_z$ for aqueous solutions of PEG$_{800}$-AuNPs with different nanoparticle concentrations (0.05 – 10 nM) in the presence of 0.5 mM K$_2$CO$_3$. Intensities are displayed on logarithmic scales. (b) Horizontal linecut profiles along $Q_{xy}$ direction at $Q_z = 0.020$ Å$^{-1}$ integrated over $Q_z$ range $5 \times 10^{-3}$ Å$^{-1}$ at low $Q_{xy}$ range (0.02–0.07Å$^{-1}$) from GISAXS patterns in (a). The plots are vertically shifted for clarity.

**Estimated surface coverage of crystalline PEG-AuNP superlattices**

Here, we estimate the maximum in the electron density (ED) of monolayers of 2D crystalline PEG-AuNPs based on a space filling model using the known EDs of water and pure Au, and the 2D crystalline structures determined by GISAXS. We then compare our calculated maximum ED to the one obtained from the X-ray reflectivity to estimate the macroscopic surface coverage of the 2D crystalline PEG-AuNPs.

![Schematic of a nanoparticle monolayer at the vapor-liquid interface with corresponding ED profile along surface-normal direction, associated with the sectional view at the maximum ED position.](image)

We assume that in the mono-particle layer of the 2D crystalline, all AuNPs are perfectly packed in the same plane, leading to a maximum ED at the plane occupied by the centers of AuNPs as illustrated in Fig. S6a. The corresponding sectional view at the maximum ED position is shown in Fig. S6b. In this maximum ED plane, the area fraction of AuNPs in the unit cell of a 2D hexagonal crystalline is $\phi = A_{np}/A_{2D}$, where the area occupied by an AuNP is $A_{np} = \pi D^2/4$, and the area of a 2D unit cell with a lattice constant $a_L$ is $A_{2D} = a_L^2 \sqrt{3}/2$. The ED of pure gold is $\rho_{Au} = 79 \rho N_A/M_{Au} = 4.66$ e/Å$^3$, where $\rho = 19.3$ g/cm$^3$, $N_A = 6.02 \times 10^{23}$ mol$^{-1}$ and $M_{Au} = 196.97$ g/mol are bulk gold density, Avogadro number and atomic weight of gold, respectively. The ED of subphase area surrounding the AuNPs ($\rho_{sub}$) is considered as ED of pure K$_2$CO$_3$ solution with the same concentration to the bulk (contribution of the PEG shell to the ED is the same as that of surrounding media, which is justified by our SAXS results; see Fig. S2). Assuming that K$_2$CO$_3$ solids dissolved in pure water increase the ED of aqueous solution without changing the solution volume, the ED of K$_2$CO$_3$ solution at the concentration...
Table S1 Maximum electron density of 2D PEG-AuNP superlattices at the vapor-liquid interface

<table>
<thead>
<tr>
<th>MW of PEG (nM)</th>
<th>[PEG-AuNPs] (n_s)</th>
<th>([K_2CO_3]) (M)</th>
<th>Lattice constant (a_0) (Å)</th>
<th>ρ(K_2CO_3) (e/Å(^3))</th>
<th>ED of (K_2CO_3) solution (\rho_{2Dmax}) (e/Å(^3))</th>
<th>Estimated maximum ED (\rho_{max}) (e/Å(^3))</th>
<th>Maximum ED extracted from XRR (\rho_{max}) (e/Å(^3))</th>
<th>Estimated surface coverage (\psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6000</td>
<td>5</td>
<td>0.005</td>
<td>388 ± 4</td>
<td>0.3342</td>
<td>0.532–0.540</td>
<td>~0.531</td>
<td>≥96 %</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>5</td>
<td>0.05</td>
<td>336 ± 5</td>
<td>0.3360</td>
<td>0.557–0.569</td>
<td>~0.557</td>
<td>≥95 %</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>5</td>
<td>0.5</td>
<td>322 ± 3</td>
<td>0.3545</td>
<td>0.641–0.652</td>
<td>~0.645</td>
<td>≥98 %</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>5</td>
<td>1</td>
<td>245 ± 2</td>
<td>0.3749</td>
<td>0.868–0.885</td>
<td>~0.695</td>
<td>≥95 %</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>2.5</td>
<td>0.5</td>
<td>338 ± 4</td>
<td>0.3545</td>
<td>0.613–0.626</td>
<td>~0.589</td>
<td>≥87 %</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>10</td>
<td>0.5</td>
<td>309 ± 3</td>
<td>0.3545</td>
<td>0.665–0.677</td>
<td>~0.617</td>
<td>≥81 %</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>5</td>
<td>1</td>
<td>149 ± 1</td>
<td>0.3749</td>
<td>1.712–1.749</td>
<td>~1.322</td>
<td>≥90 %</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>10</td>
<td>0.5</td>
<td>158 ± 3</td>
<td>0.3545</td>
<td>1.551–1.581</td>
<td>~1.783</td>
<td>≥100 %</td>
<td></td>
</tr>
</tbody>
</table>

of \(c\) (in Molar) is estimated to be \(\rho_{K_2CO_3} = \rho_w + 68cN_A/10^{27} = 0.334 + 0.0410c\) e/Å\(^3\). Using the space filling model, the maximum ED of 2D crystalline structure is \(\rho_{2Dmax} = \rho_{Au}\Phi + \rho_{sub}(1 - \Phi)\). The calculated maximum ED results are summarized in Table S1 below. Overall, the estimates are close to the results measured by XRR. Applying the calculated \(\rho_{2Dmax}\) and the measured maximum ED \(\rho_{max}\) extracted from XRR, the surface coverage of 2D crystalline is \(\psi = (\rho_{max} - \rho_{sub})/(\rho_{2Dmax} - \rho_{sub})\) (See Table S1). The surface coverage is nearly 100 %. We note that in this simple model the surface coverage of 2D crystalline is underestimated owing to the assumption of perfect lateral packing of AuNPs in the same plane and the negligence of surface roughness.

Hydrodynamic size of AuNPs and PEG-AuNPs in salts

Using dynamic light scattering we estimate the hydrodynamic size of bare and PEG-capped particles. Unlike polyelectrolyte-capped AuNPs (including ssDNA-AuNPs), as shown in Fig. S7, the hydrodynamic size distribution of PEG-AuNPs remains practically the same in the presence of salts. This also shows that the polymer in PEG\(_{800}\)-AuNPs is too short to behave like the theoretically infinitely long polymer brush.

Fig. S7 Dynamic light scattering (DLS) measurements of unfunctionalized AuNPs, PEG\(_{800}\)-AuNPs and PEG\(_{6k}\)-AuNPs dispersed in the bulk solution under different conditions as indicated. The AuNPs with PEG shells clearly show larger hydrodynamic size than that of the bare Au cores (unfunctionalized AuNPs). In addition, DLS results of PEG\(_{6k}\)-AuNPs with or without \(K_2CO_3\) indicate that the presence of \(K_2CO_3\) in the solution (up to 0.5 M) have little effect on the hydrodynamic size of nanoparticles in the bulk.

Grafting density of PEG on AuNPs
Thermogravimetric analysis (TGA) is used to estimate the grafting density of PEG on AuNPs. The concentrated PEG-AuNPs is dried at 60 °C for 4 hours prior to TGA measurements. The TGA is carried out under a nitrogen atmosphere from 25 to 800 °C at a ramp rate of 10 °C/min. The weight loss between 300 °C and 450 °C corresponds to the thermal degradation of the PEG. For instance, the weight loss of PEG2k-AuNPs as function of temperature is shown in Fig. S8. The weight percentage at 300 °C and 450 °C are 94.66 % and 61.96 %, respectively. Therefore, 32.70 % of weight is related to the PEG loaded on AuNPs, and 61.96 % of weight is from pure AuNPs. The weight of each AuNP is 

$$m_{np} = \frac{\rho \pi D^3}{6},$$

where \(\rho = 19.3 \text{ g/cm}^3\) is bulk gold density, \(D = 8.8 \pm 0.9 \text{ nm}\) is the diameter of the AuNP. The molecular weight of PEG2k is \(m_{PEG} = 6000\). Thus, the number of PEG2k per AuNP is

$$n = \frac{32.70 m_{np}}{61.96 m_{PEG}} = 367.$$ 

The grafting density is

$$\sigma = n / (\pi D^2) = 1.51 \text{ chains/nm}^2.$$ 

**Theoretical Model**

**Physical parameters of PEG**

There is a considerable range of values for the Kuhn length, Flory characteristic ratio \(C_n\) and Kuhn monomer mass \(M_0\) in the literature. The values used here are calculated from Mark and Flory\(^4\), who report the values for PEG (also called PEO) in salt at the \(\theta\)-point, the exact conditions analyzed in this paper, as

$$\langle r^2 \rangle / ml^2 = C_n = 4.1(0.4), \quad (S1)$$

where \(\langle r^2 \rangle\) is the mean square unperturbed end-to-end distance for a real chain, \(l^2 = (2l_{co}^2 + l_{cc}^2)/3.0\) and \(l_{co} = 1.43 \text{ Å}, l_{cc} = 1.53 \text{ Å}\) are the O–C and C–C bond lengths, and \(m = 3 N_r\) is the number of bonds and \(N_r\) is the number of C–C–O groups in the polymer. The maximum extension of a PEO chain is therefore

$$R_{max} = (2l_{co} + l_{cc}) \cos(\theta/2)N_r = 3.64N_r \quad (\text{Å}), \quad (S2)$$

where \(\theta = 68^\circ\) is the bond angle, which is the same for all three atoms in the monomer. The Kuhn length is\(^47\)

$$b = \frac{C_n l^2 m}{R_{max}} = 7.24 \quad (\text{Å}) \quad (S3)$$

and the equivalent number of monomers of a Gaussian chain is

$$N = \frac{R_{max}^2}{C_n ml^2} = 0.503N_r \quad (S4).$$

Using that the molecular weight of a PEO monomer is \(M_1 = 2M_C + M_O + 4M_H = 44.052\), it is

$$M_0 = M_1 / 0.503 = 87.6. \quad (S5)$$
Thus for the two PEO used in this paper, the number of independent Kuhn monomers is

\[ N_{\text{6k}} = \frac{6000}{87.6} = 68.5 \ (N_r = 136) \]  
\[ N_{\text{800}} = \frac{800}{87.6} = 9.13 \ (N_r = 18) . \]

For the PEG\textsubscript{800}, the approximation \( C_n \approx C_\infty \) is certainly questionable, and explains the larger hydrodynamic radius than the theoretical estimate.

**PEG-AuNPs in solution**

As described in Refs.\textsuperscript{30,31} the three component system water-salt-PEG typically separates into two phases, an all PEG solvated by liquid A and liquid B. Liquid A consists of water and a relatively low salt concentration (a few percent weight or less), and liquid B with a higher salt concentration of ten percent or more. Early efforts to predict the phase diagram of this three component system showed a limited success\textsuperscript{50,51} as it was noted that there is a specific salt-PEG interaction, presumably through the ether oxygens and the salt cations. Therefore, we consider a model where the salt is implicit, based on the following assumptions:

- Liquid A is a \( \theta \)-solvent for PEG.
- Liquid B is a poor solvent for PEG.
- When equilibrium is established, an interface between liquid A and liquid B is formed with surface tension \( \gamma_{AB} \).

The first assumption is justified as liquid A is the phase boundary for PEG. The second assumption follows from the fact that no PEG is found in liquid Refs.\textsuperscript{30,31}.

We consider a PEG-AuNP as consisting of \( n \) flexible chains with \( N \) monomers covalently grafted at the surface of the nanoparticle core, whose radius is \( R \). The grafting density is thus \( \sigma = n/4\pi R^2 \). We first treat PEG-AuNPs in solution and then its crystallization at the interface.

**Fig. S9** Depiction of PEG-AuNP brush, and the parameters used.

Following Ref.\textsuperscript{46}, we consider PEG as gaussian chains with three-body interactions at the \( \theta \)-point (first assumption). The monomer density at a distance \( r \) from the center is given (for \( r > R \))

\[ \phi(r) = \frac{R}{r} (\sigma b^2)^{1/2} (2w_0)^{-1/4} , \]

where \( b \) is the Kuhn length, \( \sigma \) is the grafting density and \( w_0 \) is the dimensionless three-body interaction. The spherical radii \( R_h \) is obtained by imposing that the integral of the above density is equal to the total number of monomers \( = Nnb^3 \), leading

\[ \left( \frac{R_h}{R} \right)^2 = 1 + 2 \frac{N}{R_h/b} (\sigma b^2)^{1/2} (2w_0)^{1/4} . \]
For future reference, we will also need the free energy for the spherical brush at the $\theta$ point. It is given as

$$f_r = 4\pi \left( \frac{R}{b} \right)^3 (\sigma b^2)^{3/2} (2w_0)^{1/4} \log(1 + 2 N R^2 b (\sigma b^2)^{1/2} (2w_0)^{1/4}). \quad (S10)$$

To this free energy, there is an additional term that arises from the surface tension between polymer/liquid A and liquid B. We will assume that liquid B is a slightly poor solvent for PEG. This latter condition is defined by $\xi (r = R_b) < \xi_T$, where $\xi (r = r / R \sqrt{\sigma}$ and $\xi_T = b / (2\chi - 1)$ is the thermal correlation length$^{47}$, and $\chi > 1 / 2$ parameterizes the quality of solvent B to PEG. In the opposite limit $\xi (r = R_b) > \xi_T$, which is not discussed here, PEG would collapse into globules, and the size of the PEG-AuNPs is not described by Eq. S8.

The actual energy of a single nanoparticle is given as

$$\gamma = \gamma_{AB} A \pi R_b^2.$$ \quad (S11)

Based on general arguments, we expect $\gamma_{AB} \approx k_B T (2\chi - 1)^2 / b^2$.

Finally, because the PEG-AuNPs are in solution, there is the ideal term

$$F_i = N_i k_B T (\log(n_i v_0) - 1), \quad (S12)$$

where $N_i$ is the number of PEG-AuNPs in solution and $n_i = N_i / V$ its number density. The chemical potential of the bulk PEG-AuNPs is given by

$$\mu_B = \frac{\partial F}{\partial N_i} = f_r + f_s + k_B T \log(n_i v_0). \quad (S13)$$

### PEG-AuNPs at the interface

At the interface, the free energy of the PEG-AuNPs is modified in three ways: the brushes are compressed, the surface area of contact with solvent B is much reduced, and finally, there is a reduction of translational entropy.

The stretching energy of two compressed brushes has been authoritative reviewed in Ref. $^{48}$. Unfortunately, no simple expression is available for the experimental conditions, and a full calculation is beyond the scope of this paper. Therefore, we opt for a more heuristic derivation, based on the modified Derjaguin approximation for the excess free energy

$$F_e(z) = 2\pi R^2 (R + z) \int_z^{R_0} \frac{(H - f(H))}{(R + H)^2} dH \equiv 2\pi R^2 (R + z) \int_z^{R_0} \frac{\Delta f(H)}{(R + H)^2} dH. \quad (S14)$$

Here, $2(R + z)$ is the center-to-center distance of the two brushes and $H_0 = R_b - R$ is the uncompressed brush height. The quantity $f(H)$ is the free energy per unit area of a uniformly compressed spherical brush at a radius $H < H_0$. It is given as

$$\Delta f(y) = \frac{R}{b} (\sigma b^2)^{3/2} (2w_0)^{1/4} \frac{1}{b^2} G(y), \quad (S15)$$

where $y = (R + z) / R_b$. Note that the function $G(x)$ satisfies that $G'(1) = 0$, $G''(1) \approx 32.6 > 0$, and the latter condition is the statement that the uncompressed brush is a minimum of the free energy. Detailed derivations for these results will be published elsewhere. The actual potential between two PEG-AuNPs is then given as

$$F_e(z) = 2\pi \left( \frac{R}{b} \right)^3 (\sigma b^2)^{3/2} (2w_0)^{1/4} y H(y), \quad (S16)$$

where $H(y) = \int_y^1 \frac{dw}{G(w)}$, and $G(y)$ has been defined in the previous equation. Note that $H(1) = H'(1) = H''(1) = 0$. For small compressions, $1 - y \ll 1$, the above expression reduces to

$$F_e(z) = 2\pi \left( \frac{R}{b} \right)^3 (\sigma b^2)^{3/2} (2w_0)^{1/4} y \frac{G'(1)}{6} (1 - y)^3. \quad (S17)$$

It should be noted, however, that the exact formula shows that the approximation Eq. S17 has a small range of applicability as the resulting potential quickly picks up significant non-harmonic contributions for $y \lesssim 0.85$.

We assume that the surface in contact with solvent B is the area of the plane occupied by the PEG-AuNPs at the interface. The free energy of a single nanoparticle is given as

$$F_i(z) = \gamma_{AB} 2\sqrt{3} (R + z)^2. \quad (S18)$$

Finally, the entropic term is given, within dynamic lattice theory (DLT)$^{49}$.

$$F_d(z) = k_B T \{ g(R_b) + \log(v_0) \}, \quad (S19)$$

where $g(z) = \frac{1}{2N} \log \left| \det \left( \frac{D_{ij}}{\sqrt{N}} \right) \right|$, where $N_i$ is the number of particles at the interface and $D_{ij}$ is the dynamical matrix. Although it is possible to calculate the above determinant exactly for an hexagonal two dimensional lattice, the formula is excessively complex. We
therefore make the free volume approximation

$$ F_d(z) = k_B T \log(v_0/(4\pi z^2 R_h^3/3)) . $$

(S20)

The chemical potential of the PEG-Au at the interface is given by

$$ \mu_I = F_s(z) + qF_e(z) + F_v + k_B T \log(v_0/(4\pi z^2 R_h^3/3)) . $$

(S21)

**Equilibrium condition**

The condition of equilibrium between bulk and interface leads to the equation

$$ \mu_I = \mu_B , $$

(S22)

or, in explicit form:

$$ (4\pi - 2\sqrt{3}) \frac{\gamma_{AB}}{k_B T} R_h^2 \log(n_v R_h^3) = -2\sqrt{3} \frac{\gamma_{AB}}{k_B T} R_h^2 (1 - y^2) + $$

$$ + 2\pi \left( \frac{R}{b} \right)^3 (\sigma b^3)^{3/2} (2w_0)^{1/4} \gamma H(y) - \log(y^2) , $$

(S23)

which determines $y$, and from it, the lattice constant $a_L$ from $y = \frac{2R - a_L}{2R}$, as a function of the physical parameters. The above equations illustrate a physical mechanism where the dramatic reduction in surface tension that occurs when particles reach the interface entirely drives the crystallization process.

For the purposes of illustrating the physical mechanism, one can assume that the reduction of surface tension is opposed by the stretching or compression energy, and that the small compression limit Eq. S17 can be applied. With these approximations, it follows:

$$ (1 - \frac{a_L}{2R_h})^3 = (4 - \frac{2\sqrt{3}}{\pi}) \frac{1}{\sigma b^2} \left( \frac{b}{R} \right)^2 \frac{6N}{qG''(1)} \frac{\gamma_{AB} b^2}{k_B T} + \frac{b/R \log(n_v y_H)}{(8\pi - 4\sqrt{3})N(\sigma b^3)^{1/2}(2w_0)^{1/4}} , $$

(S24)

where $y_H = \frac{4\pi}{3} R_h^3$.

**Quality of the solvent**

![Fig. S10](image)

**Fig. S10** Fit of the solvent quality as described below. The results are for PEG$_{6k}$-AuNPs. Clearly, the last point, corresponding to 1 M K$_2$CO$_3$ concentration, is not consistent with a simple logarithmic dependence.

From the reported values of $\frac{2R - a_L}{2R}$ (Table S1), and the assumption that the solvent quality parameter is described by the two parameter formula

$$ \frac{\gamma_{AB} b^2}{k_B T} = \tau \log(I/I_0) $$

(S25)

a fit is performed, with $I_0 = 0.0046$ M and $\tau = 0.0021$. Here $I$ is the K$_2$CO$_3$ concentration, [K$_2$CO$_3$]. Although the quality of the fit is adequate up to about 0.5 M, it illustrates that the data is consistent with a moderately poor solvent, not far from ideal. The point at the higher salt concentration illustrates that the surface tension grows more rapidly than the logarithmic fit Eq. S25 at high ionic strengths consistent with the onset of precipitates into 3D solids.