

Binary Superlattices of Gold Nanoparticles in Two Dimensions

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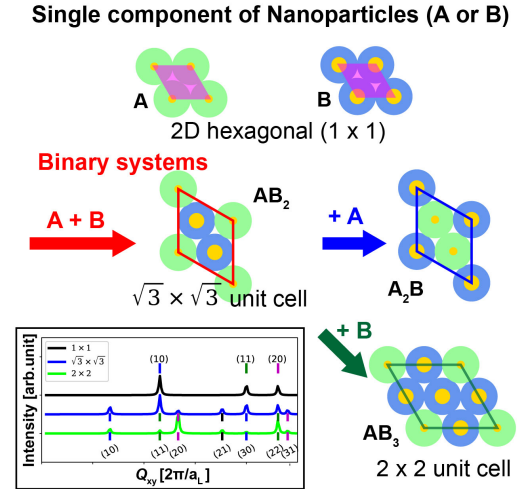
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Abstract

We have created two-dimensional (2D) binary superlattices by co-crystallizing gold nanoparticles (AuNPs) of two distinct sizes into $\sqrt{3} \times \sqrt{3}$ and 2×2 complex binary superlattices, derived from the hexagonal structures of the single components. The building blocks of these binary systems are AuNPs that are functionalized with different chain lengths of poly (ethylene glycol) (PEG). The assembly of these functionalized NPs at the air-water interface is driven by the presence of salt, causing PEG-AuNPs to migrate to the aqueous surface and assemble into a crystalline lattice. We have used liquid surface X-ray reflectivity (XR) and grazing incidence small-angle X-ray scattering (GISAXS) to examine the assembly and crystallization at the liquid interface.

TOC Graphic



Assembling nanoparticles into two- and three-dimensions (2D and 3D) ordered superlattices has been broadly employed as a route to fabricate metamaterials that can exhibit unique plasmonic and electromagnetic properties.^{1–9} Various self-assembly strategies have been developed to crystallize nanoparticles in bulk (3D

crystals) and at liquid surfaces (2D crystals). These strategies include solvent evaporation methods,^{10–14} DNA base-pairing programmable assembly,^{15–20} and polymer-polymer associations by taking advantage of hydrogen bonding and van der Waals interactions.^{21–23} The latter method has been extensively used with water-soluble polymers, such as poly ethylene glycol (PEG), poly N-isopropylacrylamide (PNIPAM), and poly acrylic acid (PAA) by grafting gold nanoparticles in suspensions, and by controlling salt, pH, and the temperature of the suspensions.^{24–31} At moderate electrolyte concentrations, PEG-AuNPs form macroscopic 2D hexagonal lattices and at higher concentrations, form short-ranged order 3D crystals.

In order to create more complex lattice types, beyond the 2D hexagonal unitary-component system, we expand our studies to binary systems. In particular, we have systematically changed the ratio of various nanoparticles of distinct sizes dissolved in bulk solutions to achieve larger and more complicated structures by varying the PEG length (molecular weight) and core particle size. Crystallization of mixed systems (binary, ternary, and higher order) are pivotal to controlling packing density of core NPs by manipulating their effective diameter by the choice of grafting.^{32,33} In this study, we have used 5 and 10 nm diameter AuNPs and grafted them with 2kDa and 5kDa PEG chains, and varied the salinity of the suspensions. The surface structures have been determined in-situ using surface sensitive synchrotron X-ray scattering methods. X-ray reflectivity (XR) and grazing incidence small-angle X-ray scattering (GISAXS) from liquid surfaces have become a major tool to determine structures at fluid interfaces as described in various publications.^{34,35}

The main reason for choosing different core AuNP sizes is to enhance the contrast between the nanoparticles in cases where co-crystallization occurs. As has been demonstrated in previous studies, the diffraction patterns of the ordered PEG-AuNPs are dominated by the AuNPs. Thus, using same size of core AuNPs can lead to negligible structure factor in the X-ray diffraction, making it diffi-

cult to distinguish between the nanoparticles.

2D assembly of the binary PEG-AuNPs systems. Single component PEG-functionalized AuNPs in suspensions can assemble into 2D hexagonal superlattices at the vapor/suspension interface. The assembly and crystallization depend on a number of factors, such as the type of salt in the suspensions (e.g., K_2CO_3 or $NaCl$), its concentration, Au core size, and PEG chain length.^{25,26,36,37} Long-range ordered 2D PEG-AuNPs assemblies at aqueous surfaces are manifested by Bragg-reflections in GISAXS patterns. Figure 1(a) shows GISAXS 2D patterns for single component PEG-AuNP suspensions and binary mixture suspension containing PEG5k-AuNP5 and PEG2k-AuNP10 in the presence of K_2CO_3 . The sharp Bragg-like diffraction rods indicate 2D crystallization of PEG-AuNPs at the vapor/suspension interface induced by the addition of K_2CO_3 . Figures 1(b–c) show line-cut GISAXS intensity profiles, integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$, as a function of Q_{xy} (see also Figure S5). For the pure PEG5k-AuNP5 and PEG2k-AuNP10, Figs. 1(b) and (c) show the diffraction patterns corresponding to 2D hexagonal structures described by Miller indices (10), (11), (20) etc. A depiction of the 2D hexagonal lattice (1×1) is shown in Figure 2(a).

Quantitative analysis of the diffraction patterns yields the lattice constant, a , for PEG5k-AuNP5 and PEG2k-AuNP10 with $a = 34.1(7)$ and $27.7(4) \text{ nm}$, respectively. These values reflect the sizes of the particles and are qualitatively consistent with the hydrodynamic diameter obtained from DLS measurements (see Figure S1). We note that the lattice constant is smaller than the hydrodynamic diameter. This is due to the effect of salt on the conformation of PEG in suspensions which renders hydrophobic characteristics to the particles and the tendency to migrate to the interface. The correlation lengths of the assembled structures (i.e., crystalline size) for PEG5k-AuNP5 and PEG2k-AuNP10 are estimated at $\sim 1 \times 10^4$ and $8 \times 10^3 \text{ \AA}$, respectively.

Formation of $\sqrt{3} \times \sqrt{3}$ binary superlattice. For a binary mixture suspension of PEG5k-AuNP5

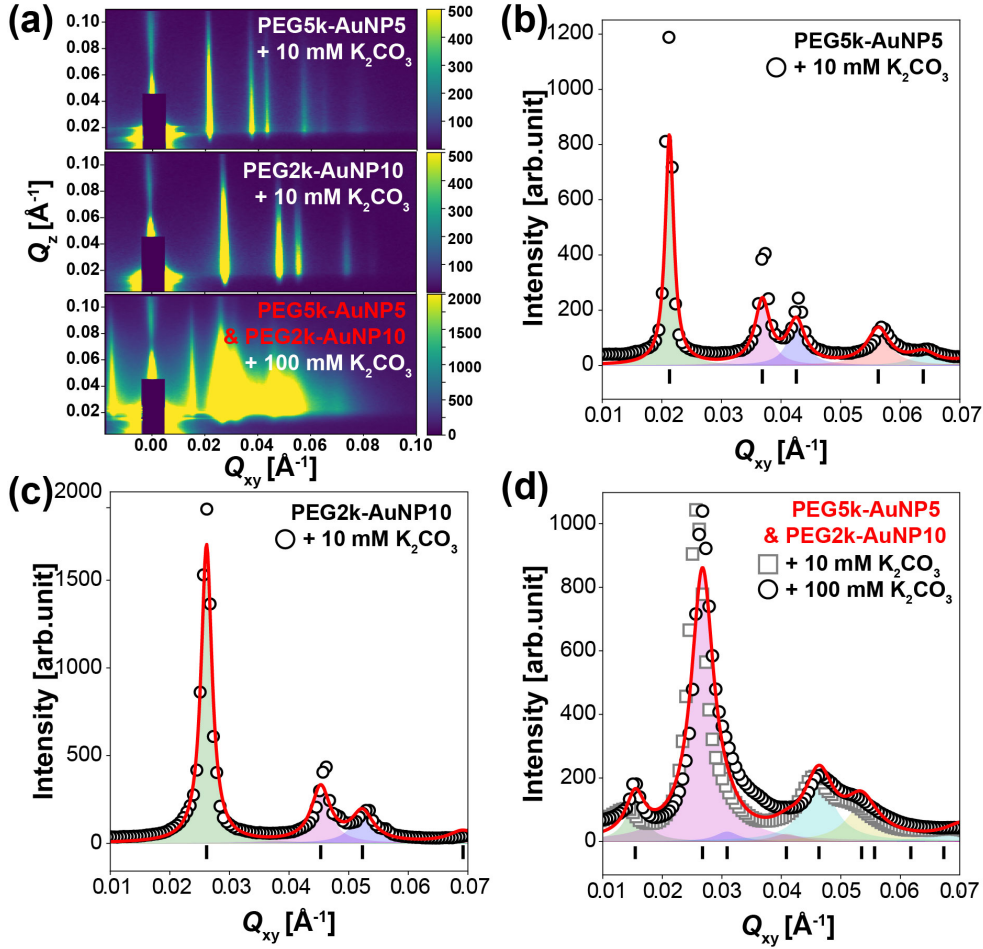


Figure 1: (a) GISAXS patterns for PEG5k-AuNP5, PEG2k-AuNP10, and mixture of PEG5k-AuNP5 and PEG2k-AuNP10 with a bulk concentration ratio of 1 : 1 in the presence of K₂CO₃, as indicated. (b – d) Line-cut intensity (integrated over $Q_z = 0.04 - 0.06$ Å⁻¹) as a function of Q_{xy} from the panels in (a), for a solution of (b) PEG5k-AuNP5 at 10 mM K₂CO₃; (c) PEG2k-AuNP10 at 10 mM K₂CO₃; and (d) PEG5k-AuNP5 mixed with PEG2k-AuNP10 with a bulk concentration ratio of 1 : 1 at 10 and 100 mM K₂CO₃. The intensity profile can be approximated with computed intensity based on the 2D nanoparticle arrangement ($\sqrt{3} \times \sqrt{3}$ lattice) in Figure 2(c). Solid red lines are best-fit profiles in terms of Eq. (S1). In (b)–(d), from left to right, the vertical bars correspond to Bragg reflections indexed as (10), (11), (20) etc. in terms of a conventional 2D hexagonal unit cell, albeit different lattice constants.

and PEG2k-AuNP10 with a bulk concentration ratio of 1 : 1 at 10 and 100 mM K₂CO₃, the diffraction pattern in Figure 1(d) exhibits a new peak at a low Q_{xy} between 0.01 and 0.02 Å⁻¹. Overall diffraction pattern in Figure 1(d) resembles that of pure PEG2k-AuNP10 shown in Figure 1(c), albeit with broader peaks. This is a strong indication that the new structure is closely related from the underlying structure of pure PEG2k-AuNP10 GISAXS pattern. We note that the new peak that emerges at low Q_{xy} is at approximately $1/\sqrt{3}$ of the (10) peak position of PEG2k-AuNP10. This strongly suggests

that the new binary structure is composed of a $\sqrt{3} \times \sqrt{3}$ lattice of the PEG2k-AuNP10 pattern as depicted in Figure 2(b). This indicates that the unit cell consists of three particles, two of PEG2k-AuNP10 (denoted as *B*, henceforth) and one of PEG5k-AuNP5 (denoted as *A*). A more in depth inspection of the new structure reveals that the *B* particles form a 2D honeycomb structure and that the *A* particle integrates into the honeycomb center (Figure 2(c)). To illustrate our result conceptually, Figure 2(a) depicts a 2D hexagonal structure comprised of the *B* particles. The expected

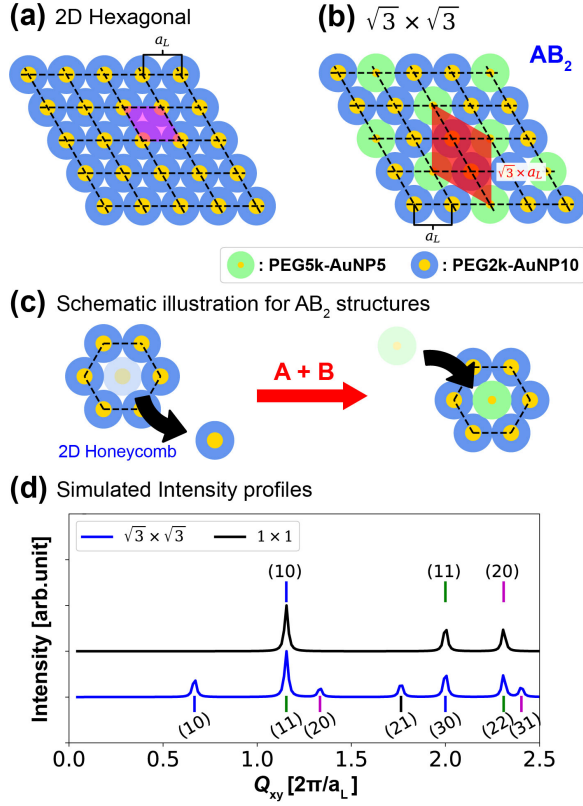


Figure 2: Illustration of two-dimensional lattices: (a) 1×1 2D hexagonal lattices where all vertices are occupied by the identical circles (core-shell entities, approximately representing nanospheres). ; (b) $\sqrt{3} \times \sqrt{3}$ 2D hexagonal lattices where the vertices are occupied by two type of circles (blue and green circles with yellow interiors represent PEG2k-AuNP10 and PEG5k-AuNP5, respectively). A unit cell is shaded in both (a) and (b). (c) Schematic illustration for the formation of $\sqrt{3} \times \sqrt{3}$ 2D hexagonal lattices. (d) Generic 2D powder diffraction simulation for 1×1 and $\sqrt{3} \times \sqrt{3}$ lattices of a finite size and resolution, assuming vacant vertices in (b) where the green circles occupy and form factors be a constant across the Q_{xy} range.

diffraction pattern for this structure is shown in Figure 2(d), taking into account the core form factor and the peak multiplicity. Figure 2(b) shows the AB_2 , $\sqrt{3} \times \sqrt{3}$ structure superimposed on the same structure as in Figure 2(a). Figure 2(c) shows how locally the particle B at the center of the hexagon is substituted by a particle A to form this structure. Figure 2(d) shows the new diffraction pattern for the $\sqrt{3} \times \sqrt{3}$ structure using the reciprocal unit of the original parent pattern, such that the (10) peak of the new structure is at the $1/\sqrt{3}$ of (10) peak of

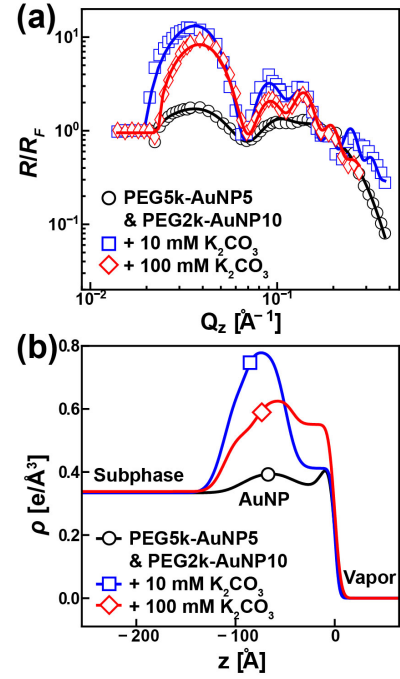


Figure 3: (a) R/R_F data for solutions mixed with PEG2k-AuNP10 and PEG5k-AuNP5 with a bulk concentration ratio of 1 : 1, at 0, 10 and 100 mM K_2CO_3 . (b) The best-fit ED profiles corresponding to the XR data in (a).

pure B structure. The (hk) peak intensity is modulated by the structure factor as given by.

$$F_{hk} = f_A + f_B \left(e^{-j2\pi(h/3+2k/3)} + e^{-j2\pi(2h/3+k/3)} \right) \quad (1)$$

Equation (1) predicts that the intensity of (10) peak, I_{10} is reduced compared to the I_{11} , as follows,

$$\frac{I_{10}}{I_{11}} = \frac{(f_A - f_B)^2}{(f_A + 2f_B)^2} \quad (2)$$

as observed experimentally (ignoring the Debye-Waller factors which is so small considering that these peaks are very close). The simulated blue intensity profile in Figure 2(d) for a $\sqrt{3} \times \sqrt{3}$ lattice provides an example of how the intensity pattern for $f_A = 0$ and f_B is a constant across the Q_{xy} range, suggesting that the GISAXS pattern from binary mixture suspensions of PEG5k-AuNP5 and PEG2k-AuNP10 is a $\sqrt{3} \times \sqrt{3}$ superlattice based on the diffraction peak positions and intensities. The data in Figure 1 are fitted using the structure

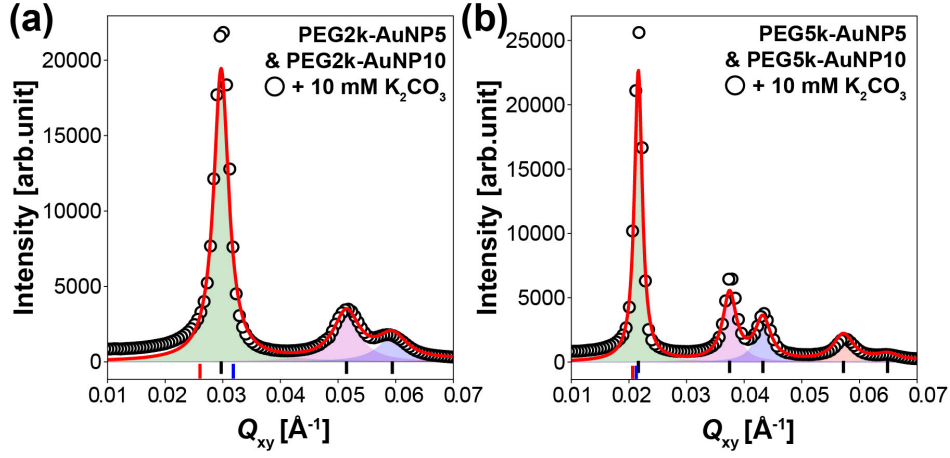


Figure 4: (a, b) Line-cut intensity (integrated over $Q_z = 0.04-0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} from a mixture of PEG2k-AuNP5/PEG2k-AuNP10 and a mixture of PEG5k-AuNP5/PEG5k-AuNP10, respectively. Red solid lines indicate its best-fit profile based on 1×1 2D hexagonal lattices. Solid lines are best-fit profiles in terms of Eq. (S1). From left to right, the black vertical bars correspond to Bragg reflections indexed as (10), (11), (20) etc. For comparison, the first Bragg diffraction peak positions from PEG-AuNP10 (red vertical bar) and PEG-AuNP5 (blue one) at 10 mM K_2CO_3 are inserted.

factors for the different structures and the form factors $f(Q)$, dominated by the AuNPs. The best-fit profile of the diffraction pattern yields a lattice constant of $47.0(1) \text{ nm}$ and an estimated crystalline size of $6.6 \times 10^3 \text{ \AA}$. Analysis of X-ray reflectivity (XR) from the same mixture suspensions shows that the co-crystallized binary system is one particle thick as shown in Figures 3(a) and (b). More detailed results and analysis of X-ray reflectivity are provided in the SI. Also provided in the SI are the actual form factors of the particles used to fit the GISAXS data.

Mixed NPs systems: variable NP size with the same PEG length. For control experiments, we mixed 2 different core sizes of AuNPs grafted with PEG with the same molecular weight. That is, we examined the following mixtures; PEG2k-AuNP5/PEG2k-AuNP10 and PEG5k-AuNP5/PEG5k-AuNP10 with a same bulk concentration ratio of 1 : 1. As we show below, these mixtures shed light on the miscibility in the assembly process of two different AuNPs that are grafted with the same PEG. We surmise that the grafted PEG renders the dominant properties of the grafted particles, more so for the longer PEG chains. Indeed, Figure 4(a) and (b) show that the diffraction pattern of these two grafted AuNPs are almost the same

as those of the pure PEG-AuNPs regardless of the Au core size. That is, the structure is dominated primarily by the grafted PEG. Nevertheless, we see small differences in diffraction patterns of parents of particles of PEG2k-AuNPs. As can be seen in Figure 4(a), the main peak of the mixture suspension of PEG2k-AuNP5 and PEG2k-AuNP10 is located between the respective (10) peak positions of PEG2k-AuNP5 (red vertical bar) and PEG2k-AuNP10 (blue one). This suggests the need to modify the grafted polymer to obtain more exotic structures.

Inverted $\sqrt{3} \times \sqrt{3}$ binary superlattice. Next, we focus on the assembly of binary mixture suspensions of PEG5k-AuNP5 (A) and PEG2k-AuNP10 (B) at several different ratios of their bulk concentrations. As shown above, for A and B that are mixed at 1 : 1 bulk concentration ratios, the resulting structure at the interface shows a 1 : 2 ratio, namely, AB_2 binary structure. Below, we explore the resulting structures for different bulk concentration ratios.

For the 2 : 1 bulk concentration ratio of A and B particles, Fig. 5(a) shows the GISAXS line-cut intensity profile displaying a similar diffraction pattern to that of the observed 1 : 1 bulk concentration ratio. That is a $AB_2 \sqrt{3} \times \sqrt{3}$ superstructure for which the particle B is still dominant (Figure 5(c), see more data in Figure

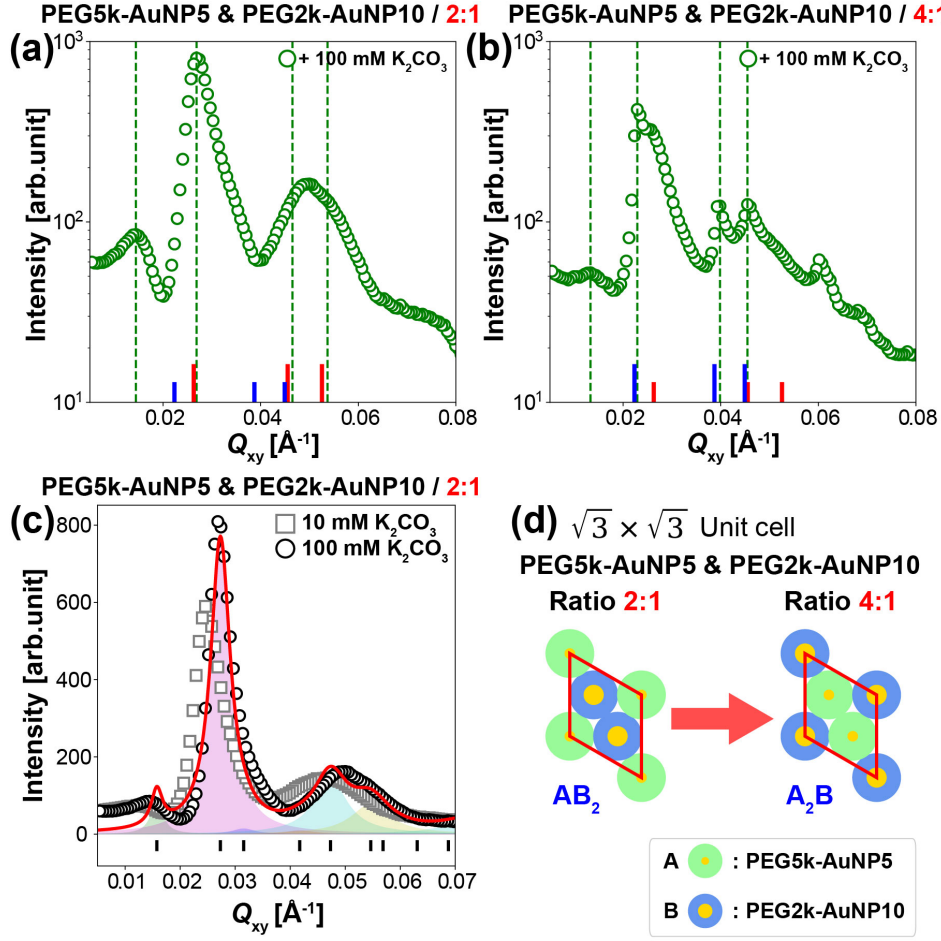


Figure 5: Line-cut intensity (integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} for a solution of PEG5k-AuNP5 mixed with PEG2k-AuNP10 with a bulk concentration ratio of (a) 2 : 1 and (b) 4 : 1 at 100 mM K_2CO_3 . Intensities are on logarithmic scales. Green dash lines are the Bragg diffraction peak positions based on $\sqrt{3} \times \sqrt{3}$ lattice. Vertical red and blue bars point to Bragg diffraction peak positions in 1×1 hexagonal lattices for PEG2k-AuNP10 and PEG5k-AuNP5 at 10 mM K_2CO_3 , respectively. The intensity profile of (a) can be approximated with the computed intensity based on the $\sqrt{3} \times \sqrt{3}$ 2D hexagonal lattices in (c). Solid lines are best-fit profiles in terms of Eq. (S1). In (c), from left to right, the vertical bars correspond to Bragg reflections indexed as (10), (11), (20) etc. (d) Schematic illustration for the transition of nanoparticle components in the $\sqrt{3} \times \sqrt{3}$ 2D hexagonal unit cell with increasing the bulk concentration ratio from 2 : 1 to 4 : 1.

S9). But for a 4 : 1 bulk concentration ratio of A and B particles, the pseudo-stoichiometry of the binary superstructure is flipped from AB_2 to A_2B , forming the inverted $\sqrt{3} \times \sqrt{3}$ binary superlattice (Figure 5(d)). The evidence supporting this is shown in Figure 5(b). The most intense peak position (the main peak on the profile, which is the second green dotted vertical line), is similar to the one from PEG5k-AuNP5 single component suspension (blue bar). The depiction of the new A_2B is shown in Figure 5(d).

Formation of 2×2 binary superlattice. For

both 1 : 2 and 1 : 4 bulk concentration ratios of A and B particles, Fig 6 shows that the newly emerging peak at low Q_{xy} position is at a ratio of $\sim 1/2$ with respect to the main peak of the pure PEG2k-AuNP10. This corresponds to a 2×2 superstructure with AB_3 pseudo-stoichiometry (illustrated in Fig 6 (a)). Figure 6(b) shows a simulation for a $\sqrt{3} \times \sqrt{3}$ and 2×2 superstructures where the fundamental peaks are distinctly separated from the most intense peaks (which are the fundamentals of parent particle peaks). We also note that the composition and structure of the binary super-

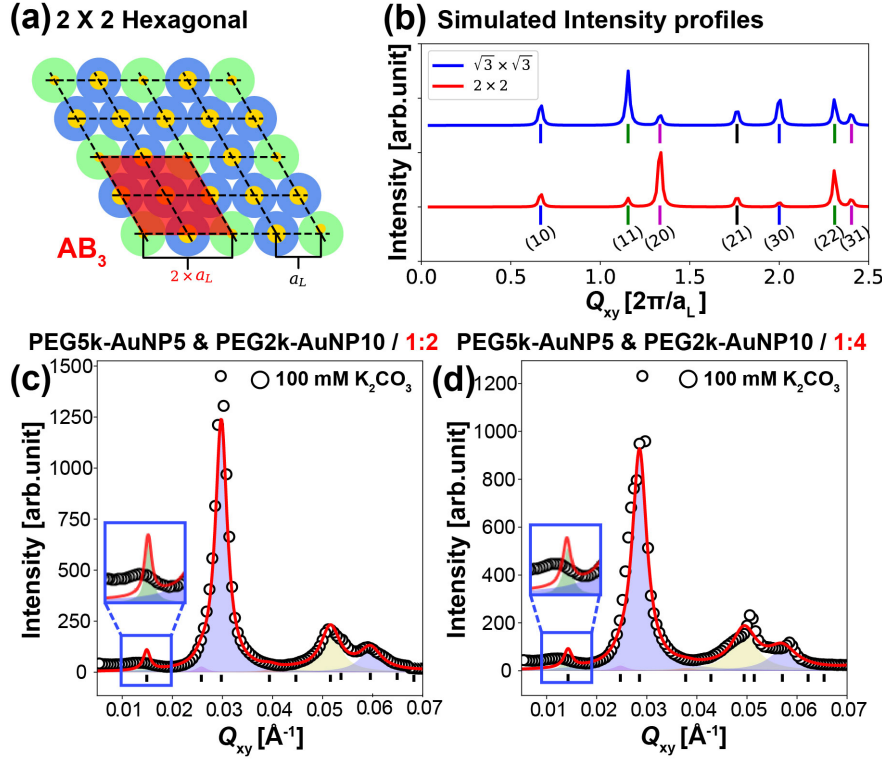


Figure 6: (a) 2×2 2D hexagonal lattices where the vertices are occupied by two type of circles (blue and green circles with yellow interiors represent PEG2k-AuNP10 and PEG5k-AuNP5, respectively) and a unit cell is shaded. (b) Generic 2D powder diffraction simulation for 2×2 lattices of a finite size and resolution, assuming vacant vertices in (a) where the green circles occupy and form factors be a constant across the Q_{xy} range. (c – d) Line-cut intensities (integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} for a solution of PEG5k-AuNP5 mixed with PEG2k-AuNP10 with a bulk concentration ratio of (c) 1 : 2 and (d) 1 : 4 at 100 mM K_2CO_3 . In both (c) and (d), red solid lines indicate their best-fit profiles based on 2×2 2D hexagonal lattices. From left to right, the vertical bars correspond to Bragg reflections indexed as (10), (11), (20) etc.

structures can be controlled by the bulk concentration ratio of the mixture PEG-AuNP components (see the data in the Figure S10). A summary of GISAXS results for the binary superlattices including lattice constant and type are listed in Table 1.

Theoretical considerations. In the following, we give a phenomenological justification for the stability of the binary superlattice against phase separation into single component phases. First we consider a system of PEG in the presence of salt with no NPs. At sufficiently high ionic strength, this system phase separates into a PEG-rich phase with almost no salt, and a salt-rich phase with almost no PEG. For PEG grafted onto AuNPs, the phase separation manifests itself by an unfavorable free-energy such that PEG-AuNP in solution migrate to the in-

terface. The AuNPs at the interface, however, are compressed, and the maximum number of AuNPs that can be accommodated at the interface in a single monolayer is limited by the size of the NPs. The experimental results are qualitatively rationalized by assuming that the larger (A) PEG-AuNPs are more readily compressed than the smaller (B) PEG-AuNPs (see some evidence in SI, Fig. S13.). As shown above, experimentally, A_2B , AB_2 , and AB_3 binary nanoparticle superlattice (BNSL) are observed. For the discussion which follows, it is important to consider the lattice constants of the single component systems, $a_A = 35.6$ and of $a_B = 27.6 \text{ nm}$ at 10 mM K_2CO_3 concentration.

The A particles are more easily compressible than the B particles (see the SI), the lattice constant is determined by a_B . Then a BNSL

with N_{WS} Wigner-Seitz cells of the type $A_l B_k$ cover an area,

$$A_{BNSL}(l, k) = \frac{\sqrt{3}}{2}(l + k)a_B^2 N_{WS} \quad (3)$$

where there $l + k$ NPs in the unit cell where the hexagonal lattice constant is a_b since the effective diameter of the A is given by the B particles. Should this BNSL phase separate into two single component A , B superlattices, it would occupy an area

$$A_{SC}(l, k) = \frac{\sqrt{3}}{2}(la_A^2 + ka_B^2) N_{WS} . \quad (4)$$

For a given area of the entire interface, A_c , the BNSL can accommodate a larger number of nanoparticles

$$\frac{N_{BNSL}}{N_{SC}} = \frac{la_A^2 + ka_B^2}{(k + l)a_B^2} \equiv \frac{k + l/f}{k + l} > 1 \quad (5)$$

where $f = \frac{a_B^2}{a_A^2} \leq 1$ ($f = 0.601$ for experiment). This provides an argument as to why the system does not phase separate, as the binary superlattice is able to accommodate a much larger number of nanoparticles, which is a manifestation of the compressibility of the long ligands, enhanced by the large curvature of the smaller diameter of nanoparticles.

In this study, we experimentally assembled a complex 2D AB_2 , A_2B , and AB_3 binary colloidal crystals on aqueous surfaces by controlling binary AuNPs concentrations with distinct ligand PEG lengths. It has been known that the PEG-AuNPs in the single component of AuNP suspensions are assembled into 2D hexagonal superlattices (1×1) at the vapor/suspension interface. However, for the binary suspensions of PEG5k-AuNP5 mixed with PEG2k-AuNP10, a larger unit cell of $\sqrt{3} \times \sqrt{3}$ hexagonal superlattice is formed, which is consistent with simulated GISAXS patterns. Furthermore, we find that the binary superlattice can be modified by controlling a bulk concentration ratio of PEG-AuNP components in mixture suspensions. For other ratios, we find the inverted $\sqrt{3} \times \sqrt{3}$ and 2×2 binary superlattices. We remark that in contrast to binary superlattices obtained from

Table 1: Summary of GISAXS results for the binary superlattices of the mixture PEG-AuNP suspensions at the vapor/suspension interface

Mixture suspensions			[K ₂ CO ₃]	a^*	Lattice
Component A	Component B	A:B	(mM)	(nm)	type
PEG5k-AuNP5	PEG2k-AuNP10	1 : 1	10	47.8(1)	$\sqrt{3} \times \sqrt{3}, AB_2$
			100	47.0(1)	$\sqrt{3} \times \sqrt{3}, AB_2$
PEG5k-AuNP5	PEG2k-AuNP10	2 : 1	10	50.0(2)	$\sqrt{3} \times \sqrt{3}, AB_2$
			100	46.0(1)	$\sqrt{3} \times \sqrt{3}, AB_2$
		4 : 1	10	62.4(1)**	$\sqrt{3} \times \sqrt{3}, A_2B$
			100	57.5(1)**	$\sqrt{3} \times \sqrt{3}, A_2B$
PEG5k-AuNP5	PEG2k-AuNP10	1 : 2	10	55.1(2)	$2 \times 2, AB_3$
			100	48.7(7)	$2 \times 2, AB_3$
		1 : 4	10	55.1(2)	$2 \times 2, AB_3$
			100	50.8(1)	$2 \times 2, AB_3$
PEG5k-AuNP5	PEG5k-AuNP10	1 : 1	10	33.4(5)	1×1 , hcp
			100	31.7(7)	1×1 , hcp
PEG2k-AuNP5	PEG2k-AuNP10	1 : 1	10	24.4(5)	1×1 , hcp
			100	24.0(6)	1×1 , hcp
Single component of AuNP suspensions					
PEG5k-AuNP5		1 : 0	10	34.1(7)	1×1 , hcp
PEG2k-AuNP5		1 : 0	10	22.8(4)	1×1 , hcp
	PEG5k-AuNP10	0 : 1	10	35.1(5)	1×1 , hcp
	PEG2k-AuNP10	0 : 1	10	27.7(4)	1×1 , hcp

* Lattice constant for the binary superlattice obtained from the profile-fitting as shown in Figures 1, and 4–6.

** Obtained from the indexed peak positions.

solvent evaporation,² the PEG-AuNP are not described by hard spheres with additional vortices,^{33,38} but are swollen with solvent and presumably no salt.

Methods

Nanoparticle characterization. Gold nanoparticle (AuNP) suspensions stabilized with citrate were purchased from Ted Pella. Thiolated polyethylene glycol (mPEG) of various molecular weights (MW) was obtained from Creative PEGWorks. AuNPs were functionalized with mPEG through a ligand exchange method.³⁷ ~ 15 nM PEG-functionalized AuNPs (PEG-AuNPs) were obtained and confirmed by the dynamic light scattering (DLS) and UV-visible spectroscopy (see Figure S1). Thermogravimetric analysis (TGA) was used to determine the grafting density of PEG-AuNPs (see Figure S2). PEG x -AuNP y denotes the AuNPs of diameter y nm grafted with PEG of molecular weight x Da. A unitary suspension of PEG-AuNPs refers to a specific (x, y) set while a binary solution refers to two non-identical sets of (x, y) for PEG x -AuNP y mixed in solution. In this study, $x = 2$, and 5k; and $y = 5$ and 10.

X-ray experimental setup. In-situ liquid surface X-ray scattering (X-ray energy $E = 9.7$ keV, wavelength $\lambda = 1.278$ Å) were conducted at the SMI beamline Open Platform Liquid Scattering (OPLS) end station, at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. X-ray reflectivity (XR) was used to determine the density profile of the surface-bound NPs across the interface. The reflected and scattered X-rays from the samples were recorded as a function of scattering vector $\mathbf{Q}$, which was defined as $\mathbf{k}_f - \mathbf{k}_i$, $\mathbf{k}_f$ and $\mathbf{k}_i$ being the wave-vector of reflected and incident X-rays beams, respectively. The reflectivity, R , was normalized to R_F , that is the Fresnel reflectivity calculated for the corresponding sample solutions, R/R_F . The best-fit to the reflectivity using Parratt’s recursive method,^{34,39} yielded the electron density (ED) profile across the interface that can be associated with the arrangement of the particles at the interface. More detailed account of X-ray experiments on liquid surfaces and interfaces is described elsewhere.^{34,35}

Grazing incidence small-angle X-ray scattering (GISAXS) was used to determine the lateral ordering of the interfacial NPs by using Pilatus 100k and 300k (Dectris) detector located 1500 mm from the sample. The GISAXS intensities were displayed as 2D images as functions of Q_{xy} and Q_z , where Q_{xy} is the in-plane component of the scattering vector $\mathbf{Q}$ and Q_z is the normal component. A line-cut of GISAXS yielded I_{1D} (i.e., $\int I_{2D}(Q_{xy}, Q_z) dQ_z$) over a specified the Q_z range as indicated in the text (see more details in SI).^{25,40,41}

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxx/yyyyy

The SI includes the following: (1) Dynamic Light Scattering data; (2) Thermogravimetric analysis; (3) Reflectivity analysis; (4) Grazing-incidence small-angle X-ray scattering analysis and simulation; (5) Theoretical considerations.

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Supporting information

Binary Superlattices of Gold Nanoparticles in Two Dimensions

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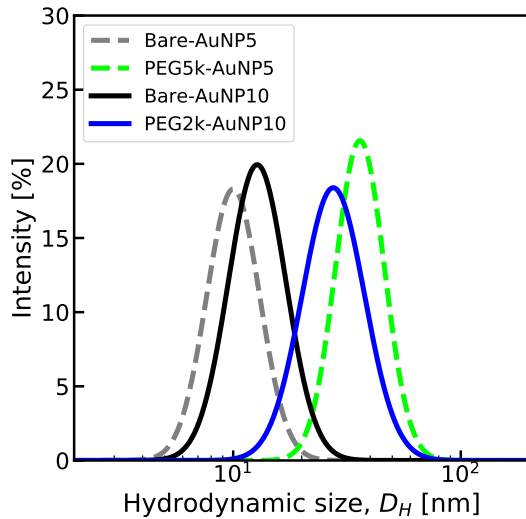
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Dynamic Light Scattering



PEG MW [Da]	AuNP diameter [nm]	D_H [nm]
-	5	9.7(3)
2,000	5	23.7(4)
5,000	5	36.4(3)
-	10	13.0(4)
2,000	10	27.5(1)
5,000	10	38.9(2)

Figure S1 & Table S1: DLS data for AuNPs before and after PEG functionalization.

Dynamic light scattering (DLS) results show the hydrodynamic size (D_H) for AuNPs before and after functionalization of PEG. Hydrodynamic size is increased with the PEG chain length (or alternatively, molecular weight) as expected. The hydrodynamic size for bare-AuNP (13 nm) is a bit larger than its nominal size (~ 10 nm), as prepared it is stabilized with citrate and that are likely bound to AuNP surfaces and increases its hydrodynamic size compared to its nominal size. Form factor is determined from SAXS measurement reflects better the nominal size of AuNPs.

Thermogravimetric analysis

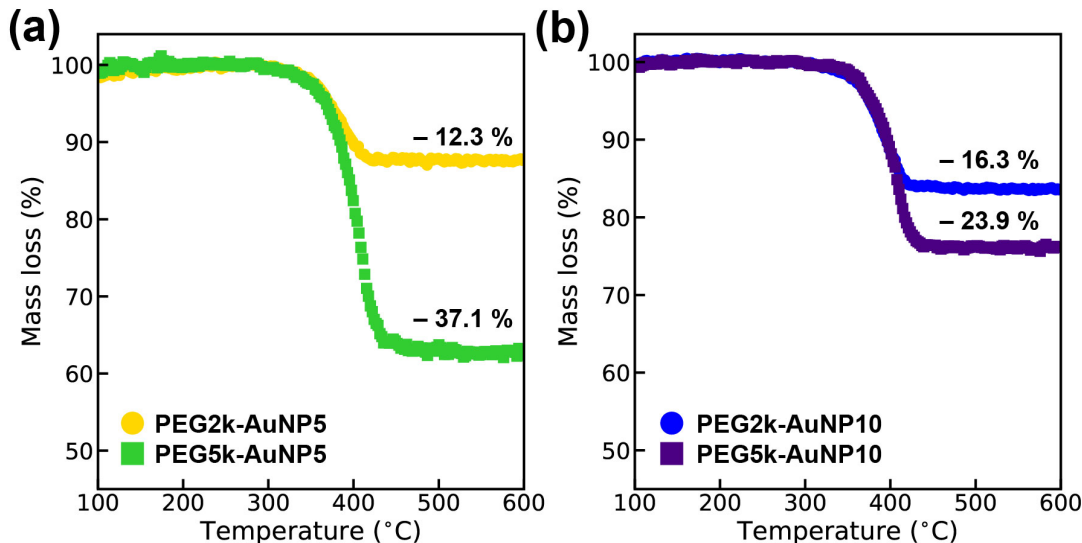


Figure S2: TGA data for PEG-AuNPs.

Thermogravimetric analysis (TGA) is conducted to estimate the grafting density of PEG-AuNPs. Functionalized PEG on AuNP surfaces are thermally degraded between 350 to 450 Celsius under nitrogen environment. The grafting densities of PEG2k-AuNP5, PEG5k-AuNP5, PEG2k-AuNP10, and PEG5k-AuNP10 are estimated to be 1.67, 2.79, 2.84, and 1.83 PEG chains/AuNP nm², respectively. Considering that PEG2k and PEG5k have ~ 43 and 111 PEG monomers, their grafting densities can be converted to 72, 310, 122, and 203 PEG monomers/AuNP nm².

Reflectivity

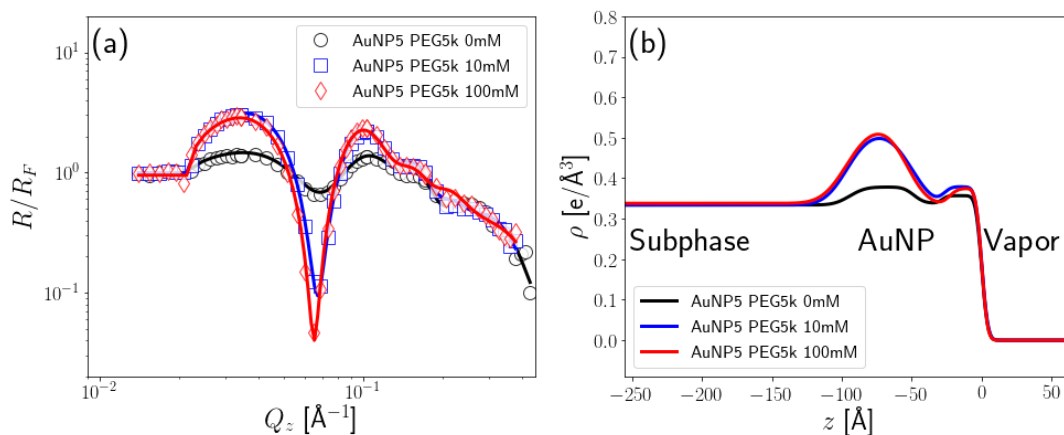


Figure S3: (a) R/R_F data for single component solutions of PEG5k-AuNP5 at $[K_2CO_3]=0, 10$ and 100 mM. (b) The best-fit ED profiles corresponding to the XR data in (a).

It has been found that PEG-functionalized AuNPs in single component suspensions migrate to the aqueous surface induced by the presence of salts in the bulk solution and then form a monolayer thick layer.^{25,26,36,37} They can be viewed as a colloidal equivalence of Gibbs monolayer of surfactants³⁰ and verified with XR methods for PEG-AuNPs of various Au core sizes and PEG lengths.^{25,26,36,37} In general, the surface enrichment of PEG-AuNPs are a function of PEG molecular

weight and particulate concentrations.^{25,37} The higher particulate concentration and longer PEG chains, the less $[\text{K}_2\text{CO}_3]$ to reach surface saturation. The population of PEG-AuNPs on aqueous surfaces varies marginally beyond the threshold salt concentrations and reaches saturation.^{25,37} Figure S3 shows an example of PEG5k-AuNP5 surface saturation beyond some threshold $[\text{K}_2\text{CO}_3]$. The interfacial ED profiles appears nearly unvaried at $[\text{K}_2\text{CO}_3] \geq 10$ mM.

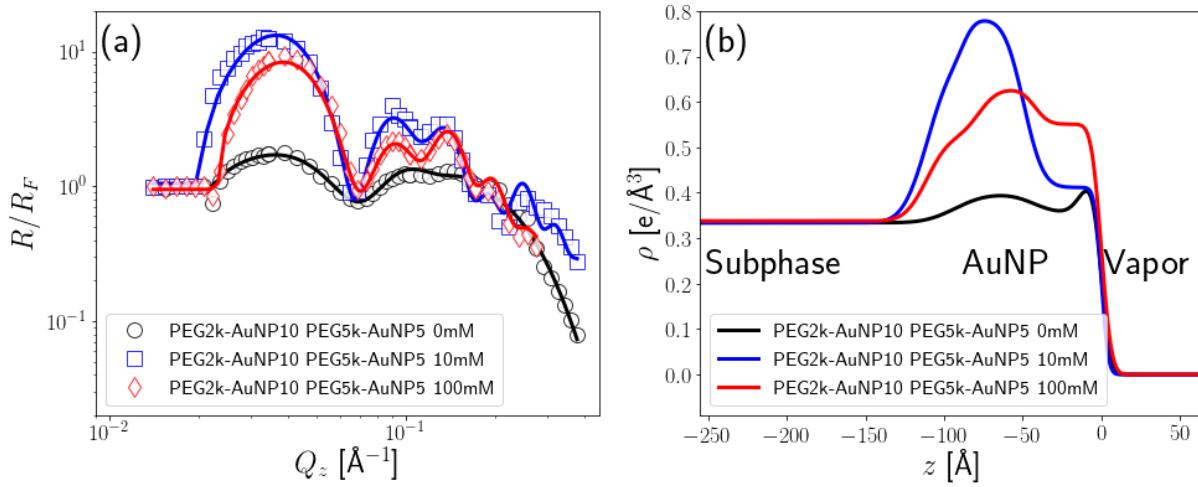


Figure S4: (a) R/R_F data for solutions mixed with PEG2k-AuNP10 and PEG5k-AuNP5 at bulk concentration ratio of 1 : 1, at 0, 10 and 100 mM K_2CO_3 . (b) The best-fit ED profiles corresponding to the XR data in (a).

Figure S4 shows the R/R_F data for binary suspensions of PEG2k-AuNP10 and PEG5k-AuNP5 at bulk concentration ratio 1 : 1 at 0, 10, and 100 mM of K_2CO_3 . The R/R_F for a bare aqueous surface features (e.g., pure water) a monotonically decreasing function of Q_z and the corresponding interfacial ED profile of $\rho(z)$ changes from a constant ED of the subphase (e.g., $0.334 \text{ e}/\text{\AA}^3$ for pure water into that of vapor (practically zero).³⁴ In the absence of K_2CO_3 , the binary suspension already yields weak interference peaks on the R/R_F profile, indicating spontaneous migration of PEG-AuNPs onto the aqueous surface. We suggest that PEG5k-AuNP5 is more likely to populate to aqueous surface more than PEG2k-AuNP10 due to the high grafting density, which is confirmed by GISAXS results. At $[\text{K}_2\text{CO}_3]=10$ mM, there are significant enhanced R/R_F ripples that suggest a highly enhanced ED region near the vapor/suspension interface corresponding to a single layer of PEG-AuNPs, in comparison with the ED profiles of pure PEG-AuNP suspensions shown in Figure S3. At $[\text{K}_2\text{CO}_3]=100$ mM, the total ED excess with respect to the subphase ED is not much altered, but the ED profiles are more skewed towards the vapor/suspension interface at $z = 0$, likely due to more aligned PEG-AuNP on the aqueous surface, as the short flat ED region appears next to the interface at $z = 0$ is presumed to be densely packed PEG-AuNPs by the shrinkage of PEG region with the increase of $[\text{K}_2\text{CO}_3]$.^{25,31,36,37}

2D GISAXS patterns

The GISAXS line-cut, as described in main text, I_{1D} , can be expressed as below:

$$I_{1D}(Q_{xy}) \propto \sum_{(h,k)} M_{hk} \cdot |\mathcal{F}_{hk}|^2 \cdot \mathcal{L}(Q_{xy}, Q_{xy}^{hk}, w_{hk}) / Q_{xy}^{hk}, \quad (S1)$$

where $\mathcal{L}(Q_{xy}, Q_{xy}^{hk}, w_{hk})$ is an area-normalized, Lorentzian function centered at Q_{xy}^{hk} with the full width at half maximum w_{hk} , to describe the peak-shape for Bragg-reflection indexed as (hk) . The crystalline domain size can also be estimated with the peak widths.^{40,41} M_{hk} represents the multiplicity of the (hk) peak assuming the 2D GISAXS originates from crystalline domains with random in-plane orientations. Q_{xy}^{hk} and M_{hk} are dictated by crystallography once the 2D lattice is specified. $\mathcal{F}_{hk}$ represents the unit cell structure factor at peak (hk) . The form factor of PEG-AuNPs, is approximated with the form factor f_D for a solid sphere of diameter D ,^{24,28,31} expressed as below

$$f_D = (\Delta\rho \cdot v) \frac{3[\sin(Q \cdot D/2) - Q \cdot R \cdot \cos(Q \cdot D/2)]}{Q^3(D/2)^3},$$

where $Q = |\mathbf{Q}| = \sqrt{Q_{xy}^2 + Q_z^2}$, $v = \pi D^3/6$, and $\Delta\rho$ is the ED difference between the AuNP and the aqueous bulk. The polydispersity of AuNPs with a mean diameter $\langle D \rangle$ and spread ΔD can be determined with small-angle X-ray scattering (SAXS),²⁴ i.e., the apparent form factor f is $\langle f^2 \rangle^{1/2}$ where $\langle f^2 \rangle = \int f_D^2 \cdot g(D) dD$. The $\langle f^2 \rangle$ is further averaged over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$ for direct comparison of experimental GISAXS data. The particulate radii distribution function adopted here, $g(D)$, is a Gaussian distribution function with the mean $\langle D \rangle$ and standard deviation ΔD .²⁴

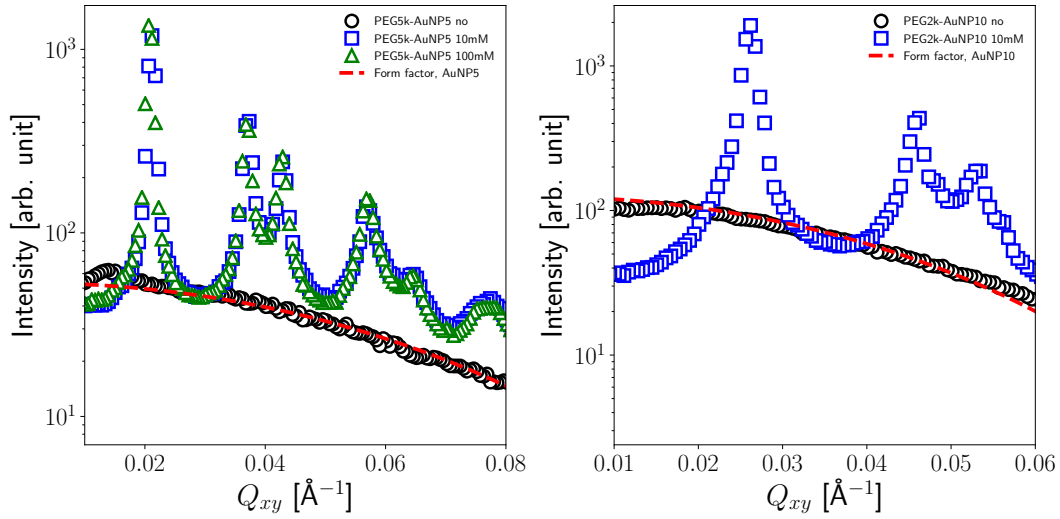


Figure S5: Line-cut intensity (integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} for a solution of (a) PEG5k-AuNP5 and (b) PEG2k-AuNP10 at various K_2CO_3 concentrations, as indicated. Intensities are on logarithmic scales. Red dash lines indicates the computed form factor intensity profiles of AuNP5 and AuNP10.

Form factors $f(Q)$

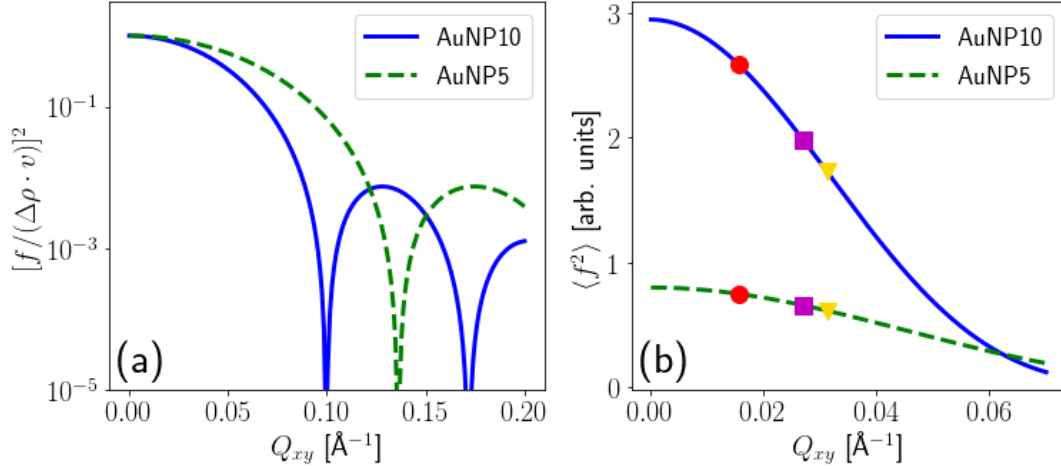


Figure S6: (a) Calculated form factor for an individual AuNP as a function of Q_{xy} at $Q_z = 0$. (b) Averaged form factor over diameter distribution and $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$. The solid symbols, circles, squares and triangles are form factors used for Q_{xy}^{10} , Q_{xy}^{11} and Q_{xy}^{20} , respectively, for binary suspension GISAXS data shown in Figure 1(c).

The nominal diameters of AuNP10 and AuNP5 are 10 nm and 5 nm, respectively. However, there is certain polydispersity (i.e., size distribution) and can be determined with small-angle X-ray scattering (SAXS).^{24,25} In this study, we used apparent diameters determined from SAXS in prior studies in evaluating GISAXS data.^{24,25,31} Based on the Gaussian distribution of AuNP in $\langle D \rangle = 9.0 \text{ nm}$ for AuNP10 and 6.6 nm for AuNP5, and $\Delta D / \langle D \rangle = 0.1$, the form factors of AuNP10 and AuNP5 as a function of Q_{xy} at $Q_z = 0$ and $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$ are computed and presented in Figure S6.

Simulation of 2D GISAXS structure factor

To validate the formula, Eq.(S1), for GISAXS line-cut profile fitting, we used simulated GISAXS intensity from a known 2D lattice of finite size. Figure S7 shows an example of 2D hexagonal lattice of a finite size consisting 4×4 unit cells with the unit cell edge length $a_L = 278 \text{ \AA}$ and oriented randomly within xy -plane. Assuming the particle attached to each unit cell is small enough so that its form factor f appears constant across the Q_{xy} of interest. To simulate the scattering intensity, $I_{\text{simu}}(Q_{xy})$, from such a 2D crystalline domain, we obtain a 2D analog of the Debye formula for powder patterns,⁴⁰ as below:

$$I_{\text{simu}}(Q_{xy}) = N|f|^2 + \sum_{p \neq q}^N f^2 J_0(Q_{xy}d_{pq}) \quad (\text{S2})$$

where d_{pq} is the center-center separation between particle p and q in the lattice consisting of total N particles. J_0 is zero-th order Bessel function of the first kind, i.e., $J_0(z) = \frac{1}{\pi} \int_0^\pi \exp(jz \cos \theta) d\theta$. Eq.S1 is used to profile-fit the generated data in terms of Eq. S2 as shown in Figure S7. The FWHM width, w_{hk} , for each peak is uniform and the reciprocal, $2\pi/w_{hk} \approx 1.1L_{\text{diag}}$, where L_{diag} is the longest diagonal of the lattice in Figure S7, consistent with the Scherrer equation.⁴⁰ For real system, there is a broadening of (hk) reflection with Q_{xy} , which is approximately $w_{hk} \propto Q_{hk}$, indicating some sort of disorder, albeit the dependence of peak width on some 2D paracrystalline disorder is much more complicated than the known dependence for one-dimensional paracrystalline disorder.⁴¹

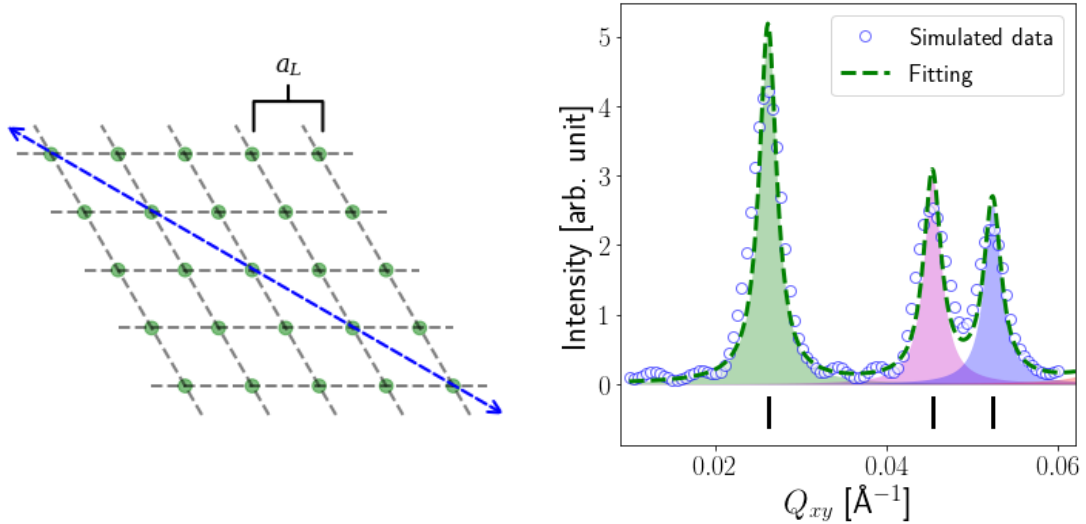


Figure S7: Left panel: A 2D hexagonal lattice of 5×5 unit cells, each of which is an equilateral rhombus of edge length $a_L = 278 \text{ \AA}$. A small particle is placed at each vertex to represent the AuNP. The dashed-line indicates the characteristic lengths of the lattice, L_{diag} , i.e., the longest length of the crystalline domain. Right panel: Simulated scattering intensity corresponding to the lattice on the left in terms of Eq.(S2), and profile-fit with Eq.(S1). The vertical bars indicates the position of Bragg-reflection at (10), (11) and (20) in terms of conventional 2D hexagonal lattice unit cell.

Other mixture suspensions of PEG-AuNPs

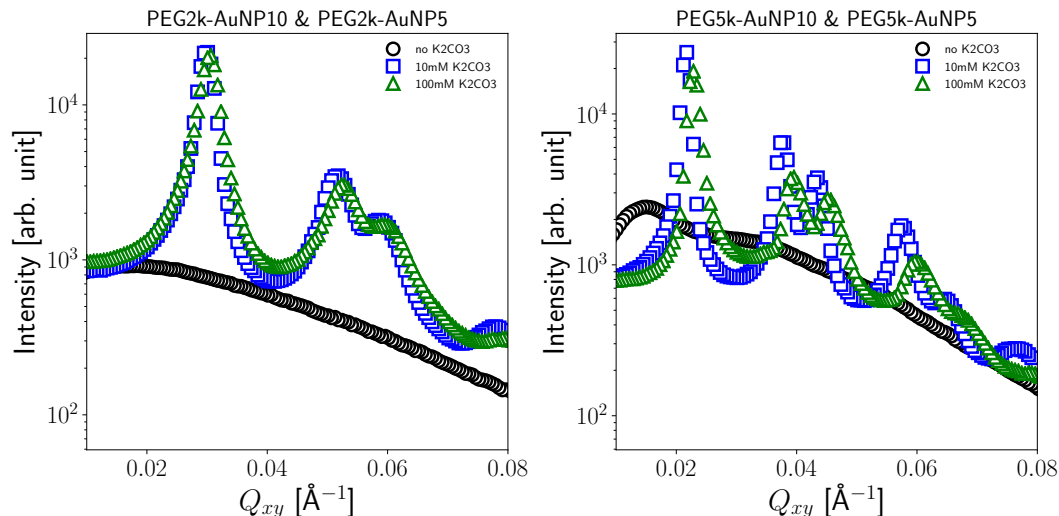


Figure S8: Line-cut intensity (integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} for mixture of PEG2k-AuNP5 and PEG2k-AuNP10 (left) and mixture of PEG5k-AuNP5 and PEG5k-AuNP10 (right) with a bulk concentration ratio of 1 : 1 at various K_2CO_3 concentrations as indicated. Intensities are on logarithmic scales.

Binary superlattices of PEG5k-AuNP5 and PEG2k-AuNP10 with different ratio

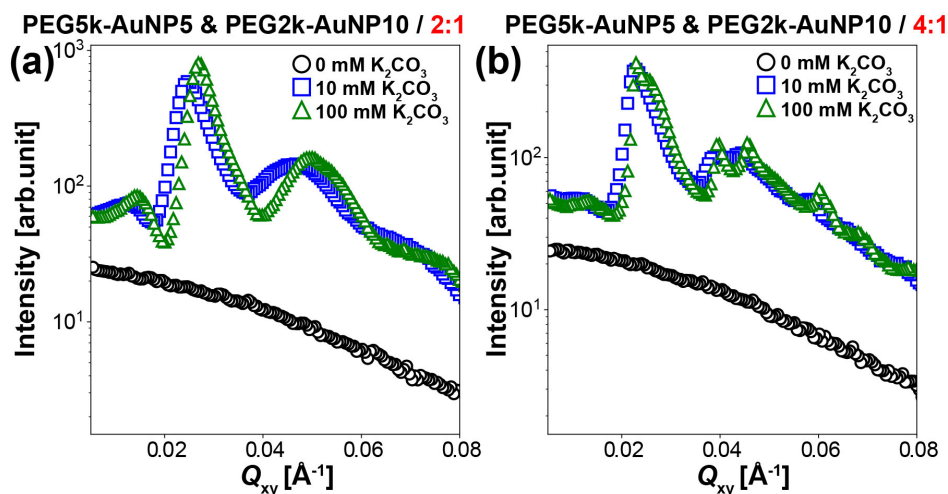


Figure S9: Line-cut intensity (integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} for a solution of PEG5k-AuNP5 mixed with PEG2k-AuNP10 with a bulk concentration ratio of (a) 2 : 1 and (b) 4 : 1 at various K_2CO_3 concentrations as indicated. Intensities are on logarithmic scales.

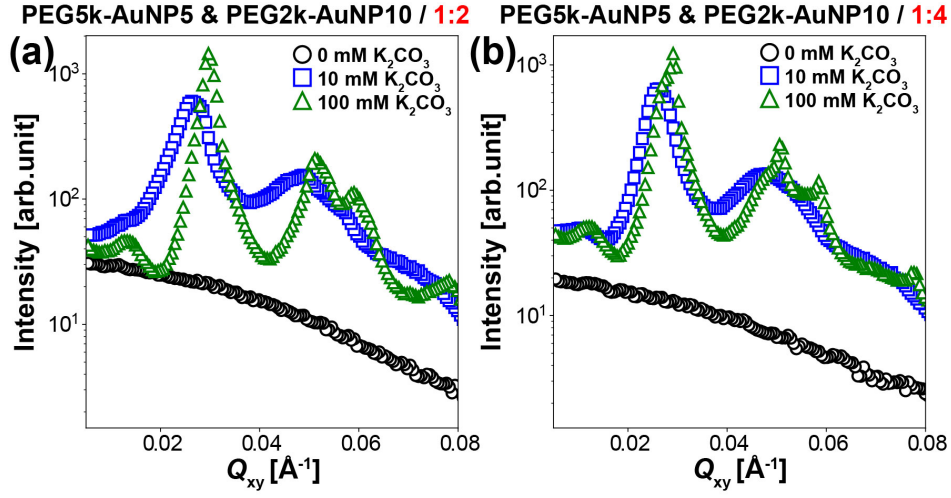


Figure S10: Line-cut intensity (integrated over $Q_z = 0.04 - 0.06 \text{ \AA}^{-1}$) as a function of Q_{xy} for a solution of PEG5k-AuNP5 mixed with PEG2k-AuNP10 with a bulk concentration ratio of (a) 1 : 2 and (b) 1 : 4 at various K_2CO_3 concentrations as indicated. Intensities are on logarithmic scales.

Theory

Notations and Parameter values

Table S2: Notation used in this study.

quantity	definition	notation
number of chains	chains per nanoparticle	$\mathcal{N}_p$
moles	number of moles	n
polymerization degree	number of monomers	N
density	mass/volume	ρ
specific volume	volume/mass	v
molar volume	volume/moles	v
number density	moles/volume	n
volume fraction	volume/volume	ϕ
molecular weight	mass/mole	M
grafting density	number of molecules/Area	σ

Following our previous studies,²⁵ the value of the different parameters are as given in Table S3.

Table S3: Parameters used

Definition	notation	value
PEO monomer length	l_P	3.64 ($\text{\AA}$)
PEO Kuhn length	b	7.24 ($\text{\AA}$)
PEO diameter factor	ν	0.584
PEO Molecular Weight	M_{PEO}	44.052 ($\text{g}\cdot\text{mol}^{-1}$)
Water molecular volume	v	29.91 ($\text{\AA}^3$)
Nanoparticle radius	R	25.0, 45.36 ($\text{\AA}$)
gold molecular weight	M_{Au}	196.97 ($\text{g}\cdot\text{mol}^{-1}$)

The nanoparticle radius is obtained from the X-ray analysis. These parameters imply

$$v_P = b^3 \nu^2 = 129.43 \text{ \AA}^3 \quad (\text{S3})$$

$$\rho_{\text{PEO}} = 10^4 \frac{M_{\text{PEO}}}{6.0221 v_P l_P} = 1124 \text{ kg} \cdot \text{m}^{-3} \quad (\text{S4})$$

$$A_c = b^2 \nu^2 = 17.88 \text{ \AA}^2 \quad (\text{S5})$$

$$N_r = \frac{M_p}{M_{\text{PEO}}} \quad (\text{S6})$$

$$N = 0.503 N_r . \quad (\text{S7})$$

and also $\rho_{\text{Au}} = 19300 \text{ kg} \cdot \text{m}^{-3}$. Here N is the number of Kuhn segments and N_r the number of actual segments. For PEG5k, PEG2k, $M_p = 5 \cdot 10^3, 2 \cdot 10^3$ and hence

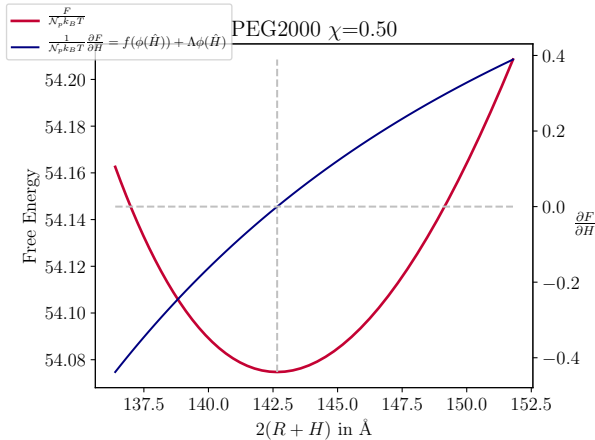
$$\begin{aligned} N^{\text{PEG5k}} &= 57.1 , & N_r^{\text{PEG5k}} &= 113.5 \\ N^{\text{PEG2k}} &= 22.8 , & N_r^{\text{PEG2k}} &= 45.4 \end{aligned} \quad (\text{S8})$$

The grafting density and number of chains per nanoparticle is

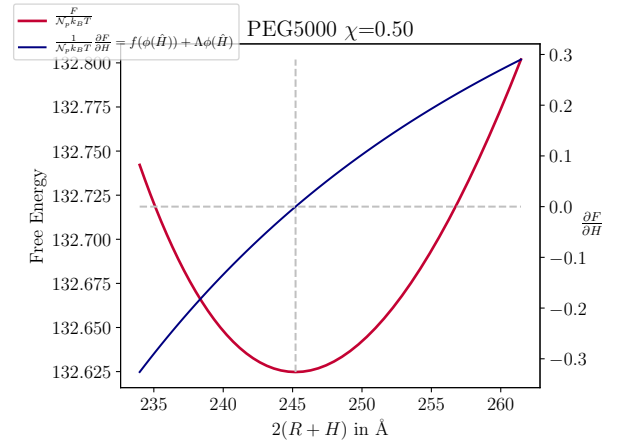
$$\begin{aligned} \sigma^{\text{PEG2k}}(D=5) &= 0.0167 \frac{\text{chains}}{\text{\AA}^2} = 1.67 \frac{\text{chains}}{\text{nm}^2} \rightarrow \mathcal{N}_p = 131 \\ \sigma^{\text{PEG5k}}(D=5) &= 0.0279 \frac{\text{chains}}{\text{\AA}^2} = 2.79 \frac{\text{chains}}{\text{nm}^2} \rightarrow \mathcal{N}_p = 220 \\ \sigma^{\text{PEG2k}}(D=10) &= 0.0284 \frac{\text{chains}}{\text{\AA}^2} = 2.84 \frac{\text{chains}}{\text{nm}^2} \rightarrow \mathcal{N}_p = 734 \\ \sigma^{\text{PEG5k}}(D=10) &= 0.0183 \frac{\text{chains}}{\text{\AA}^2} = 1.83 \frac{\text{chains}}{\text{nm}^2} \rightarrow \mathcal{N}_p = 473 \end{aligned} \quad (\text{S9})$$

these values are consistent with previous estimates.^{25,31,37}

Using the same model as introduced in Ref.^{31,37} the free energy as a function of brush diameter is shown in Fig. S11 and Fig. S12.

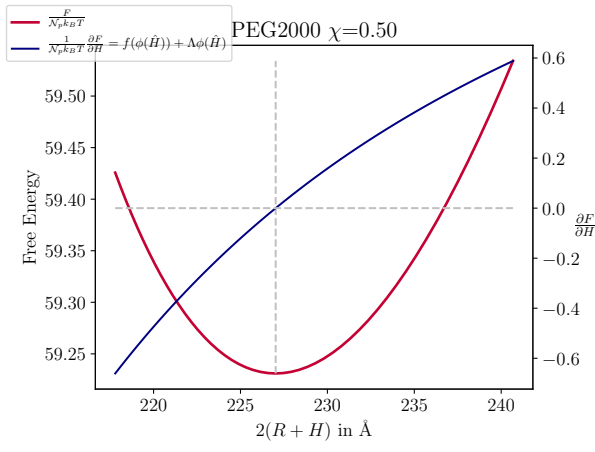


(a) Free Energy for PEG2k-AuNP5.

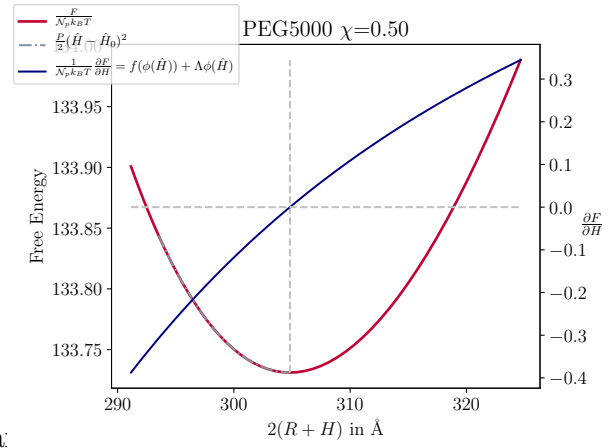


(b) Free Energy for PEG5k-AuNP5.

Figure S11: Free Energies for AuNP5



(a) Free Energy for PEG2k-AuNP10.



(b) Free Energy for PEG5k-AuNP10.

Figure S12: Free Energies for AuNP10

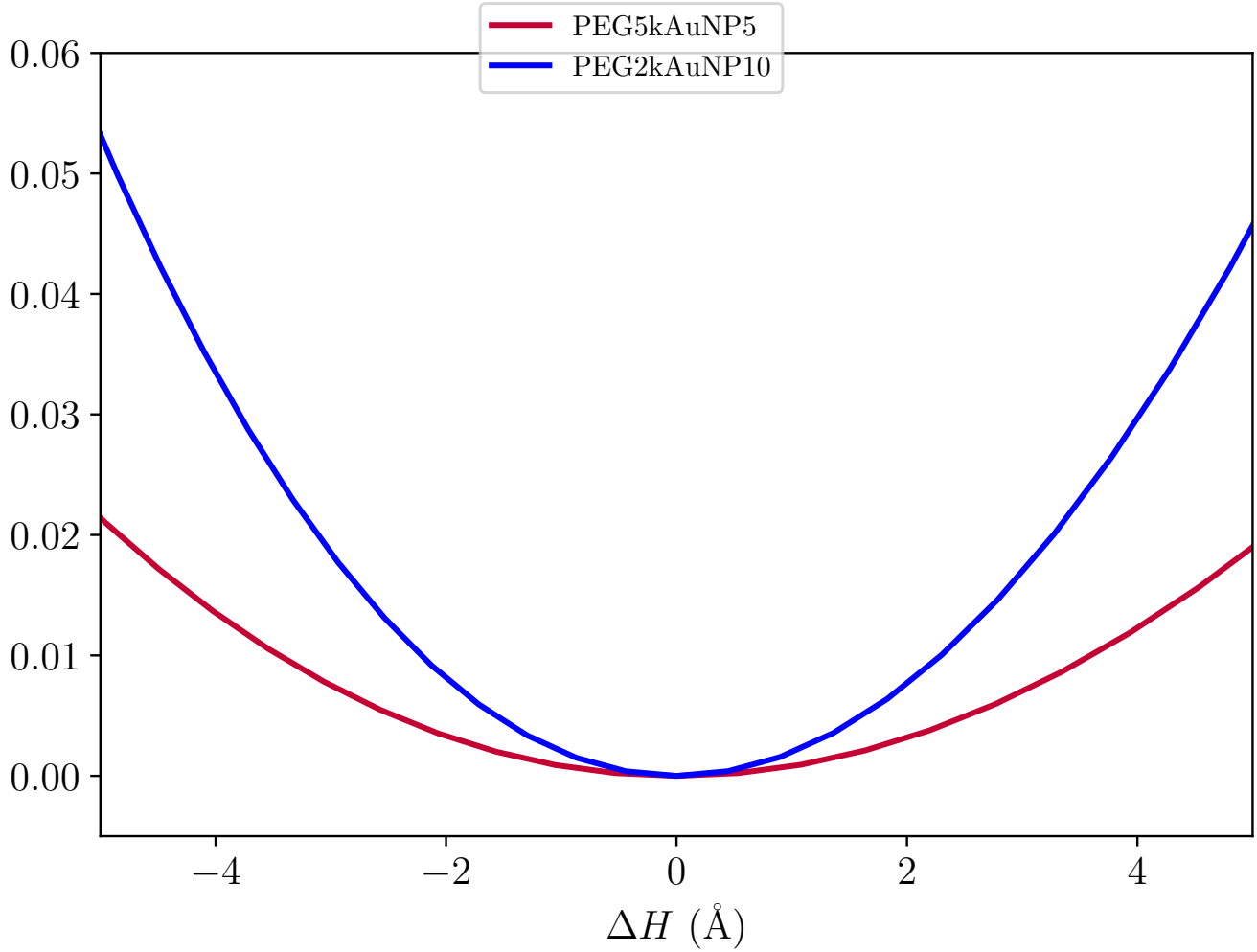


Figure S13: Comparison of the free energy for PEG5kAuNP5 and PEG2kAuNP10. $\Delta H = D - D_h$, where D is the actual diameter under compression, D_h the hydrodynamic radius.