

In order to validate the hypothesis that the metal NPs are located within the PS domains, rather than at their surface, the observed volume change of the domains can be compared with the volume occupied by the added particles.

This comparison was made through the following calculations. First, the volume of the PS domains was determined. AFM images indicate that the PS domains can be approximated as spherical caps with a height, h , of 6 nm. The radius at the base of the cap, a , can be determined from TEM images (data of Fig. 7 and Table 1) and the volume calculated from equation S.1 :

$$\text{PS domain volume} = V_{\text{PS}} = \frac{\pi h}{6} (3a^2 + h^2) \quad [\text{S.1}]$$

The volume increase resulting from the addition of NPs is given as $\Delta V_{\text{PS domains}}$.

Next, the total volume occupied by the metal NPs added to each domain was evaluated from the number of NPs per domain, N , and by considering the particles to be spheres of mean radius, r :

$$\text{Total volume of NPs in a PS domain} = V_{\text{NPs}} = \frac{N 4\pi r^3}{3} \quad [\text{S.2}]$$

The contour length of butanethiol is considered in the radius of the NPs, for an effective radius of 1.5 nm.

The average number of NPs per domain, N , has been evaluated in two ways. $N_{\text{TEM count}}$ values were determined by particle counting on TEM images with Image J analysis software. $N_{\text{calculated}}$ values were calculated from the concentration of particles (mg/mL) spread at the air-water interface. The mean mass of a single particle can be determined from the mean Au core diameter (from TEM) and the mass of ligand per NP (from TGA):

$$mass_{\text{NP}} = \frac{4}{3}\pi r^3 \rho_{\text{Au}} + mass_{\text{C}_4\text{SH}} \quad [\text{S.3}]$$

From this value, the number of spread particles can be calculated for each concentration and combined with the trough area at transfer to yield the number of particles per unit surface area. The number of PS domains per unit surface area can be determined from TEM images and the ratio of the two provides the number of NPs per PS domain ($N_{\text{calculated}}$).

Results are given in Table S.1

Table S.1 Geometric features of PS domains as a function of NP concentration in the spreading solutions and estimated total volume occupied by butanethiol coated Brust NPs

NP conc. (mg/mL)	a (nm)	$V_{\text{PS domains}}$ (nm ³)	$\Delta V_{\text{PS domains}}$ (nm ³)	N_{TEM} count	$N_{\text{calculated}}$	V_{NPs} TEM count (nm ³)	V_{NPs} calculated (nm ³)
0.0	28.0	7500		0	0		
0.5	30.0	8600	1100	70	150	1000	2100
1.0	32.5	10000	2500	110	250	1550	3500

The results indicate that the observed increase in the volume of the PS domains is of the same order of magnitude as the volume of the added particles. It is important to note that there is significant uncertainty associated with the various parameters, and, in particular, it is difficult to obtain an accurate count of the number of NPs per domain. Particle counting from TEM images yields a value for N that is about half that obtained from the concentration of the spreading solution. The TEM count underestimates the number of NPs because of limits in resolution and the fact that NP overlap can obscure some particles in the 3D domains. Conversely, the number of particles calculated from the spreading concentration constitutes an overestimate. Because the particle size distribution is not monodisperse, the true average volume of the NPs is greater than that calculated directly from the average particle radius, as in equation S.2. Furthermore, any particle aggregation, either in the spreading solution or at the air-water surface, will reduce the average number of particles per PS domain. Despite these limitations, the two methods for determining N provide upper and lower limits to a reasonable true value. Indeed, the observed increase in the size of the PS domains (ΔV_{PS}) falls between the two limiting values of V_{NPs} and is thus in agreement with the conclusion that the NPs are located within the domains.