

SUPPLEMENTARY INFORMATION

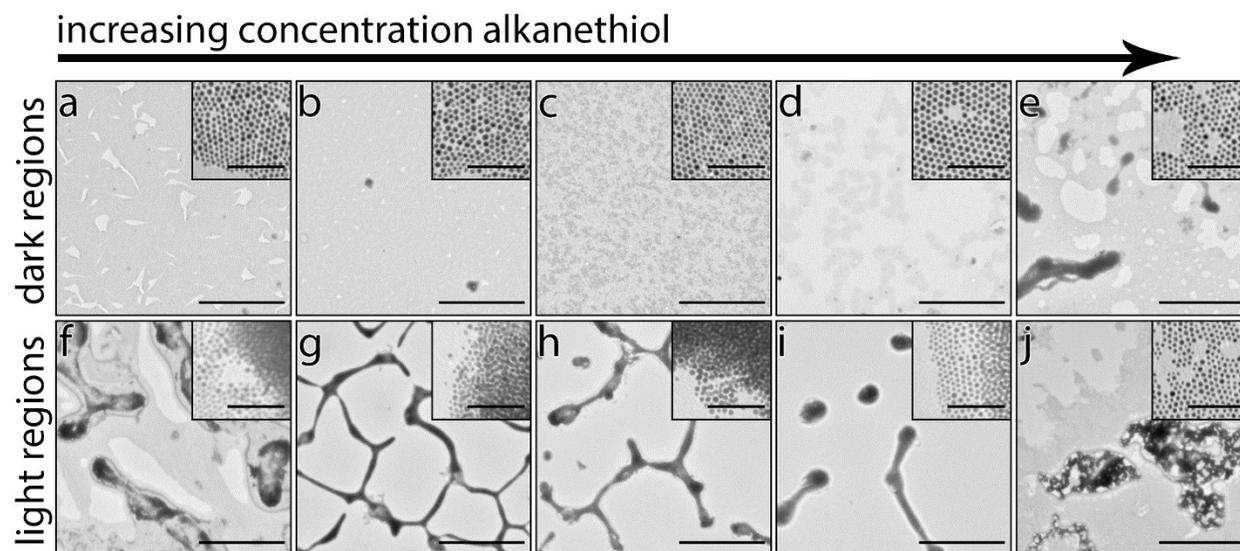


Figure 1S. TEM images for a dodecanethiol trial using the same excess thiol concentrations as in Figure 3.

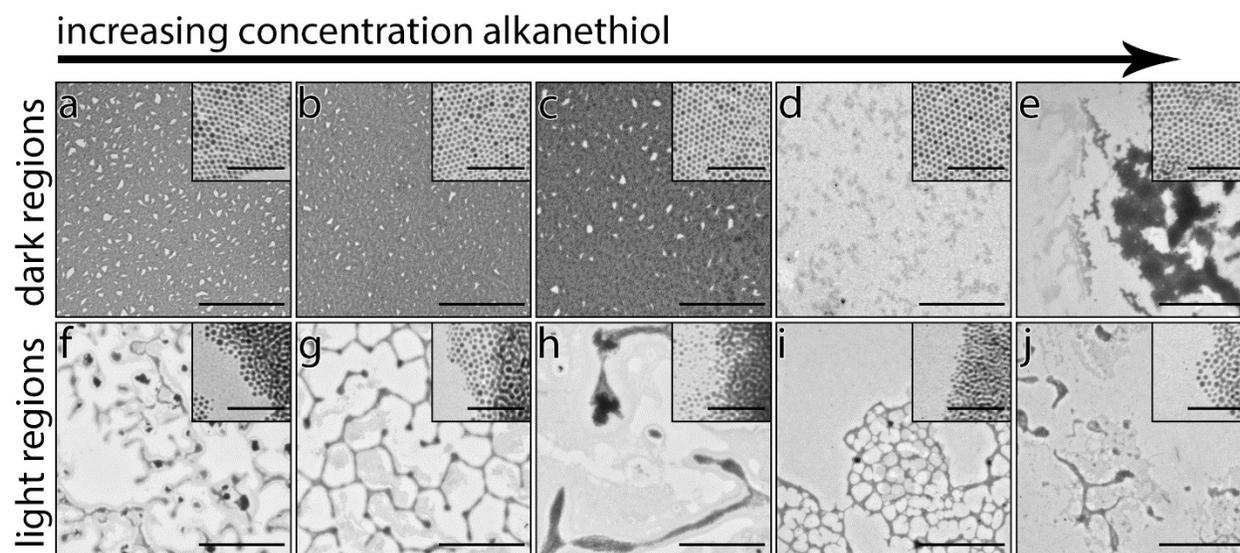


Figure 2S. TEM images for an octadecanethiol trial using the same excess thiol concentrations as in Figure 5.

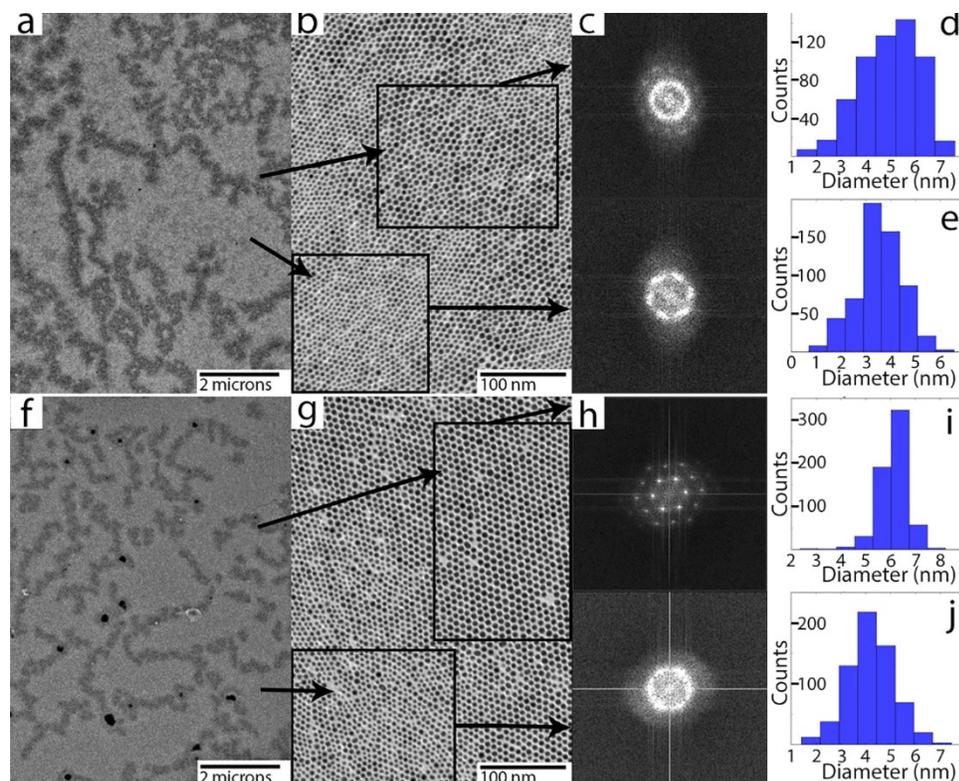


Figure 3S. TEM and fast Fourier transform (FFT) images of films obtained using excess dodecanethiol volume fractions of 2×10^{-4} ((a)-(e)) and 1×10^{-3} ((f)-(j)) in the Teflon well. Arrows and boxes indicate magnified views of regions of high and low electron transmission and their corresponding FFTs. (d) and (e) show histograms of NP diameters of NPs shown in the upper and lower boxes in (b), respectively, and analogously (i) and (j) show histograms of NP diameters corresponding to the upper and lower boxes in (g), respectively. Average particle sizes for the histograms are: (d) $5.09 \text{ nm} \pm 26\%$, (e) $3.60 \pm 24\%$, (i) $6.17 \pm 8.4\%$, (j) $4.16 \pm 22\%$.

In Figure 3s, the difference in electron transmission arises from differences in NP size. The figure shows the low/high transmission regions (Figure 3S(a) and 3S(f)), the corresponding monolayers (Figure 3S(b) and 3S(g)), 2-d Fourier spectra of the respective monolayers (Figure 3S(c) and 3S(f)), and corresponding histograms of NP diameters. Since features in the Fourier spectra for the low transmission regions are closer to the origin than those for the high transmission regions, they correspond to large particle spacing due to larger particle size. This can also be seen directly in the TEM images themselves as well as from the histograms. The

larger particles shown Figure 3S(g) in fact also exhibit hexagonally close packed order, which is confirmed by bright spots in the corresponding Fourier spectrum shown in Figure 3S(h).

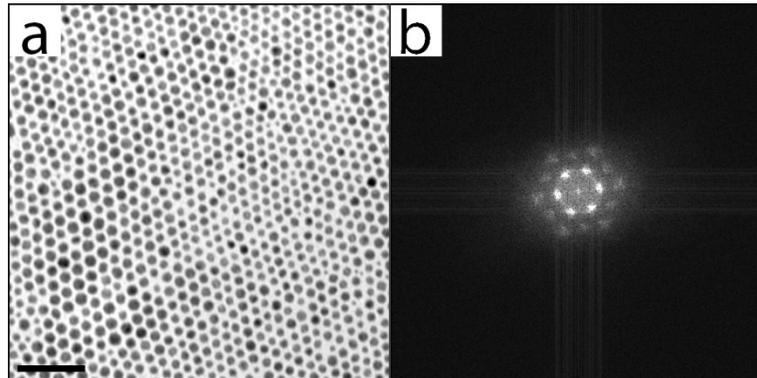


Figure 4S. TEM image (a) and corresponding FFT (b) of a dark region of a film formed using an excess octadecanethiol volume fraction of 1×10^{-3} in the Teflon well. The scale bar in (a) corresponds to 40 nm.

Figure 4S shows a TEM image of a monolayer obtained at 1×10^{-3} excess octadecanethiol concentration. The monolayer exhibits order on an approximately 200×200 nm scale; the image's 2-d Fourier spectrum shows clear peaks at multiple orders (see Figure 4S(b)).