Nanocrystal Superlattices that Exhibit Improved Order On Heating: An Example of Inverse Melting?

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Supporting Information

Volume fraction occupied by ligand in superlattices of 1.66 nm diameter octadecanethiol-capped Au nanocrystals. Using the BCC lattice parameter *a*, measured by GISAXS and the average Au core diameter measured by SAXS, V_{core}, the volume fraction occupied by the Au nanocrystal cores is: $V_{core}/V_{total} = 2 * ({}^{4}/_{3} * \pi * R^3)/a^2 = 5.6\%$. If the remaining volume in the superlattice is occupied by capping ligands (94.4%), the weight fraction of Au in the nanocrystal assemblies is: $W_{core}/W_{total} = (V_{core} * \rho_{Au})/(V_{core} * \rho_{Au} + V_{ligand} * \rho_{ligand}) = 60\%$. This is consistent with thermogravimetric analysis (TGA, Fig. S1). TGA was performed on a Mettler Toledo TGA-1, heating the nanocrystals in a 70 µL alumina crucible (Mettler Toledo) from 25°C to 800°C at a heating rate of 20°C/min. The sample was then held at 800°C for 30 min. The measurements were performed under 50 mL/min nitrogen gas flow. The weight loss of ~40% corresponds to the loss of organic ligands.

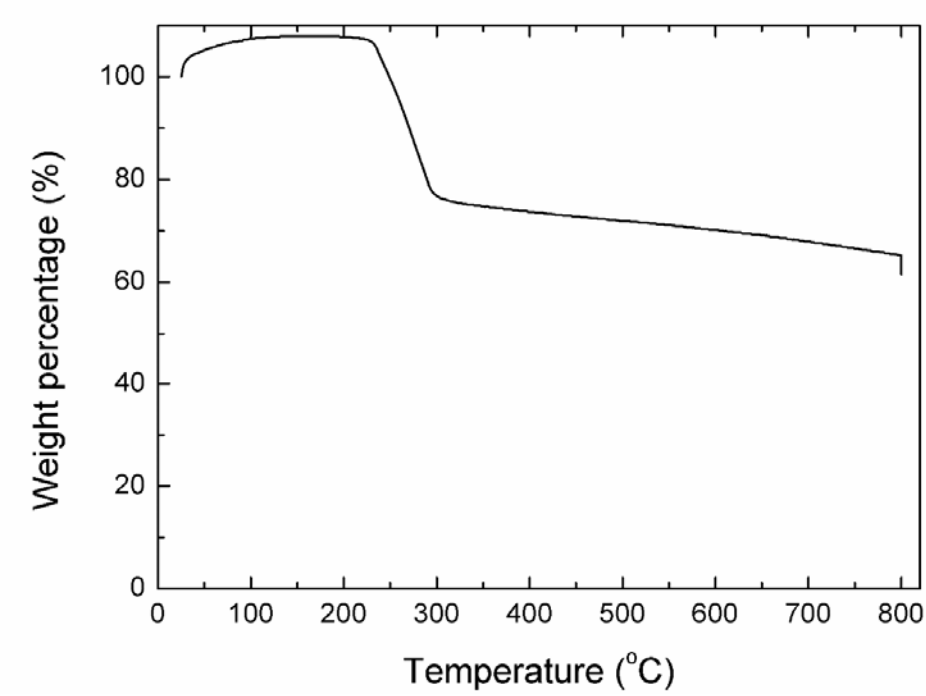

Figure S1. TGA of size-selected octadecanethiol-capped Au nanocrystals (average diameter of 1.66 ± 0.30 nm).

TEM images of the octadecanethiol-capped Au nanocrystals used in the study. Figure S2 shows TEM images of size-selected octadecanethiol-capped Au nanocrystal at high (top) and low (bottom) magnifications. The nanocrystals exhibit diameters less than 2 nm, consistent with sizing carried out be SAXS. Figure S3 shows TEM images of octadecanethiol-capped Au nanocrystals prior to size-selective precipitation. The particle size distribution is noticeably broader.

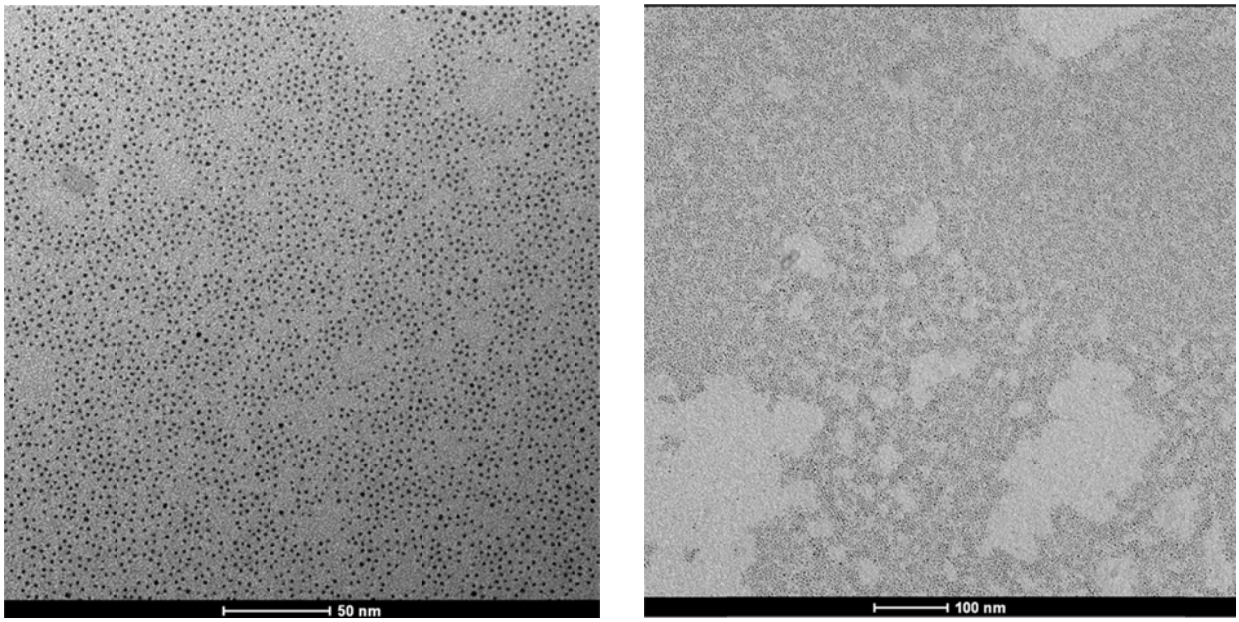

Figure S2. TEM images of size-selected octadecanethiol-capped Au nanocrystals.

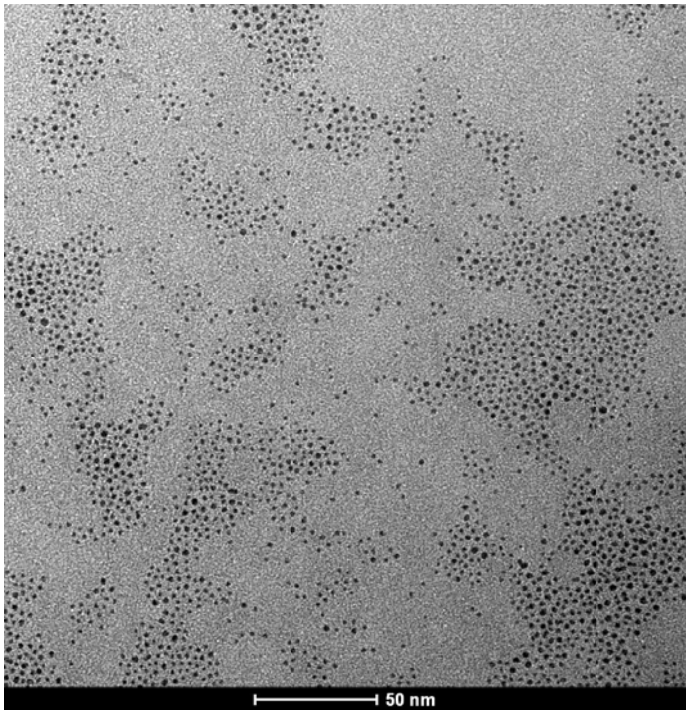

Figure S3. TEM image of octadecanethiol-capped Au nanocrystals prior to size-selective precipitation.

SAXS of octadecanethiol-capped Au nanocrystals without size selective precipitation dispersed in toluene. Solution Small-Angle X-ray Scattering (SAXS) data of octadecanethiol-capped Au nanocrystal prior to size-selective precipitation are shown in Figure S4, in which top figure is plot of intensity against q and bottom one is porod plot of the data. Fitting the solution SAXS data to a model of a collection of non-interacting solid spheres with a Gaussian size distribution reveals that these nanocrystals have an average diameter of 1.75±0.35 nm (20% polydispersity).

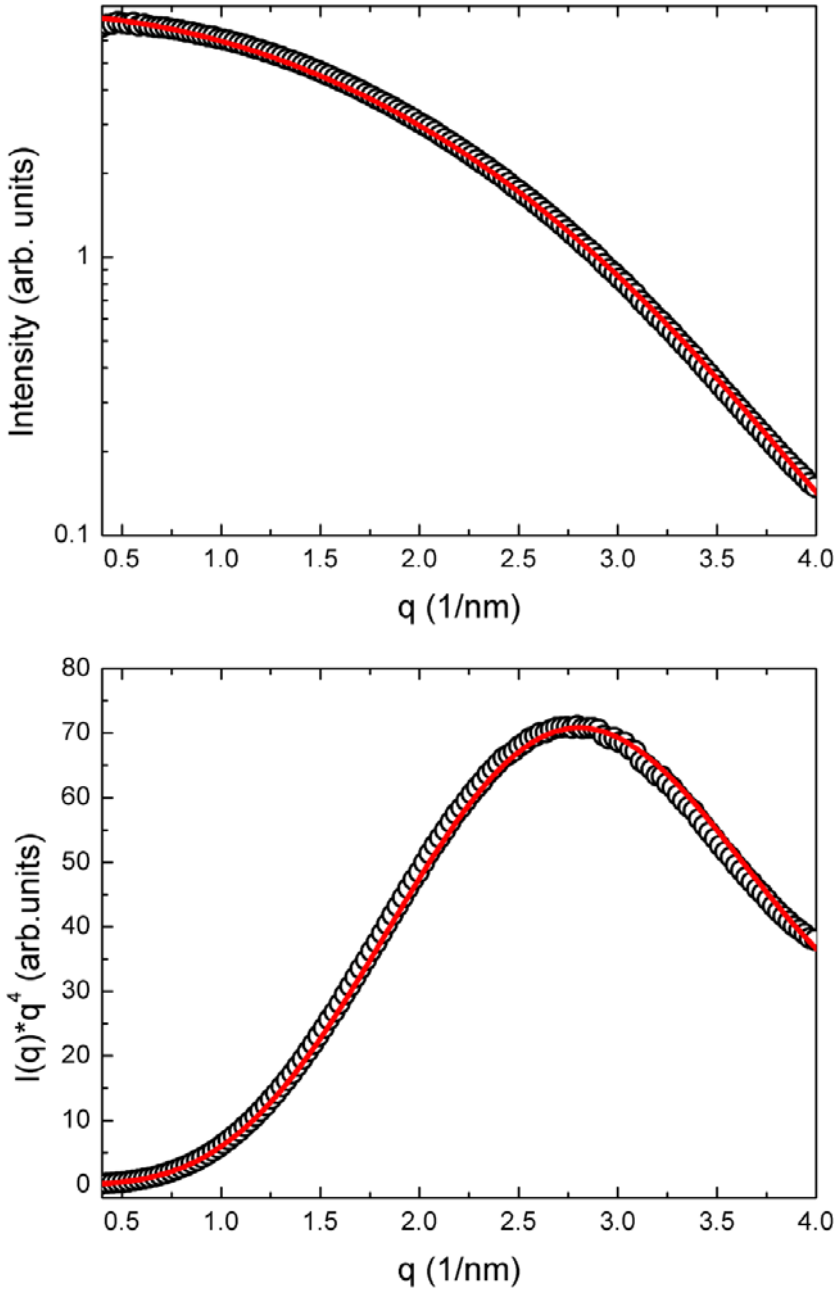

Figure S4. Solution SAXS data (black cycles) and the best fitting (red curve) of octadecanethiol-capped Au nanocrystals without size-selective precipitation. Top: Log of intensity vs *q*, Bottom: Porod plot.

Structure factor calculations. Structure factor, S(q), could be calculated from scattering profile I (q) and form factor P(qR) determined in solution SAXS:

$$I(q) = n * P(qR) * S(q),$$

$$\text{hence, } S(q) = {I(q)}/{n * P(qR)}.$$

The Normalization factor n, is determined using the factor that

$$\langle S(q)\rangle = N^{-1} * \sum_{j,k}^{N} \langle e^{-iq(R_j - R_k)}\rangle$$

approaches a value of 1 at high q.[1,2] In this work, we normalize our S(q) by assuming $S(q_{max})=1$. Figure S5 shows structure factors of Au nanocrystal superlattice during one heating-cooling cycle, plotted in 3d fashion.

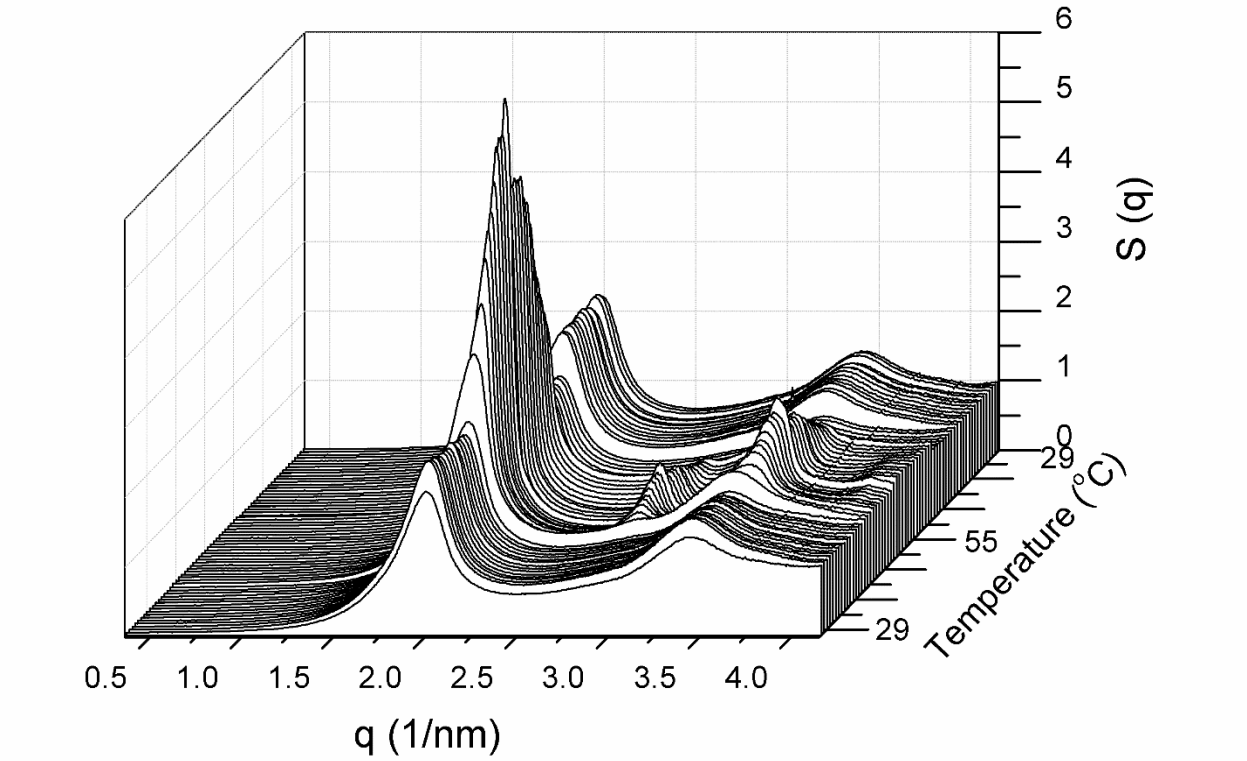

Figure S5. Structure factors of Au nanocrystal superlattice in a heating-cooling cycle.

References:

1. Cusack, N. E. The physics of structurally disordered matter: an introduction. *Philadelphia: Hilger*, **1987**.

2. Korgel, B. A.; Fitzmaurice, D. Small-angle x-ray-scattering study of silver-nanocrystal disorder-order phase transitions. *Phys. Rev. B* **1999**, *59*, 14191-14201.