Supporting Information

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SI Text

Calculation of Aggregate Size

According to the theory of diffraction, the intensity of the first order diffraction peak hkl (110 peak for BCC crystals, 111 peak for FCC crystals, 100 peak for an amorphous aggregate), I_{hkl}, is given by Eq. **1**:

$$I_{hkl} \sim N_c \cdot N_p^2 \cdot |F_{hkl}|^2, \quad [1]$$

where N_c is the number of aggregates, N_p is the number of a AuNPs in an aggregate, and F_{hkl} is the form factor of the AuNP. The volume of aggregate is defined assuming the aggregate is cubic with side length L_c.

$$V_c = (L_c)^3. \quad [2]$$

Applying the number density, ρ, of AuNPs in an aggregate results in relation 3:

$$N_p = \rho \cdot V_c. \quad [3]$$

The length of an aggregate along [hkl] is then calculated with the full-width half-maximum (FWHM) of the hkl diffraction peak, Eq. **4**:

$$L_c = 2 \cdot \pi / \Delta q_{hkl}. \quad [4]$$

Because $N_p = \rho \cdot (2\pi/\Delta q_{hkl})^3$, N_c can be calculated as Eqs. **5** and **6**:

$$N_c \sim I_{hkl}/|F_{hkl}|^2/[\rho \cdot (2\pi/\Delta q_{hkl})^3]^2 \quad [5]$$

$$N_c \sim I_{hkl}/(2\pi/\Delta q_{hkl})^6. \quad [6]$$

We can then calculate N_c and L_c using the first order diffraction peak, q_0. In our in situ measurements, the number density of AuNPs in an aggregate, ρ, is assumed to be constant. We believe this to be a reasonable assumption because the q_0 peak position is almost constant over the entire growth period. All data have been normalized by $|F_{hkl}|^2$.

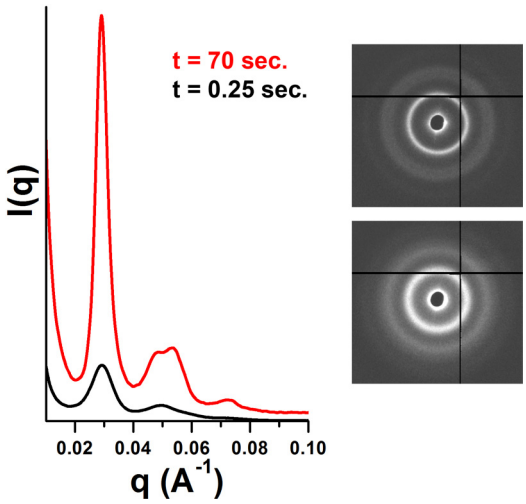

Fig. S1. Ten-nanometer short FCC scattering profiles. One-dimensional and 2-dimensional scattering profiles for the 10-nm DNA-AuNP Short FCC crystal system, taken immediately after combining the DNA-AuNPs (black trace, bottom scan) and after 70 s of annealing at 40 °C (red trace, top scan). No form factor has been subtracted from these scans.

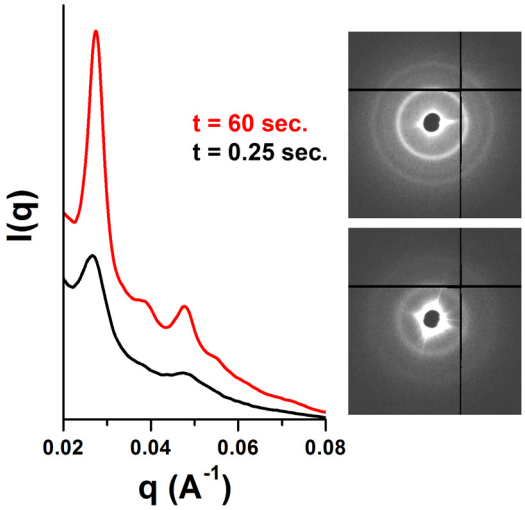

Fig. S2. Ten-nanometer BCC scattering profiles. One-dimensional and 2-dimensional scattering profiles for the 10-nm DNA-AuNP BCC crystal system, taken immediately after combining the DNA-AuNPs (black trace, bottom scan) and after 60 s of annealing at 40 °C (red trace, top scan). No form factor has been subtracted from these scans.

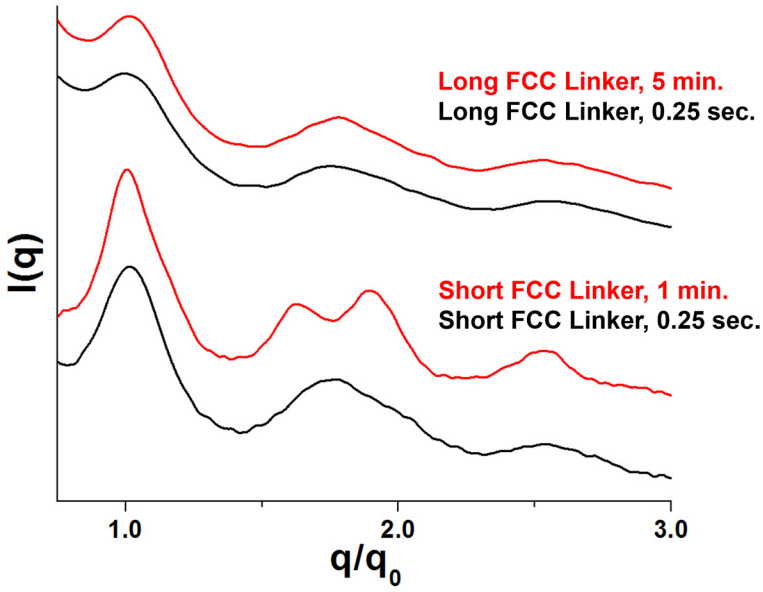

Fig. S3. Isothermal formation of short and long FCC linkers. Plots of the 1D SAXS patterns for 5-nm DNA-AuNP crystals in the short FCC and long FCC crystal systems. Note that the short FCC crystal system transitions from disordered aggregates to an FCC crystal in ≈1 min, whereas the long FCC crystal system exhibits only a slight change in structure, even after 5 min of annealing.

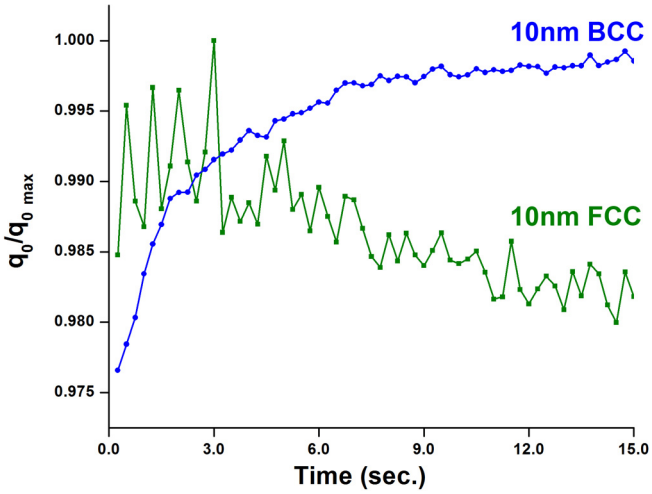

Fig. S4. Formation and reorganization of 10-nm crystals. Plots of the progression of q_0 peak position for 10-nm DNA-AuNP FCC (green trace) and BCC (blue trace) crystals. The general trends in peak position are observed to be the same as for the 5-nm DNA-AuNP crystals with the same DNA linkers. The nanoparticles in the BCC system restructure themselves over a period of $\approx$15 s, whereas the nanoparticles in the FCC system reach maximal order on a time scale unobservable because of both fast kinetics and a large degree of noise for $t < 3.0$ s. The alterations in q_0 position for the FCC crystal are attributable to slight variations in solution temperature and X-ray beam degradation of the DNA strands.

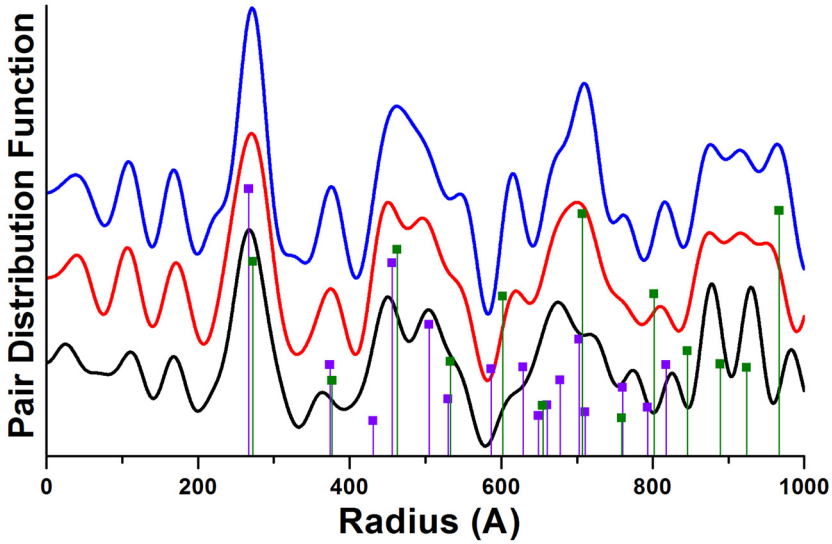

Fig. S5. Pair distribution functions for the 5-nm DNA-AuNP short FCC system. The pair distribution function is a simple Fourier transform of the normalized structure factor $S(q)$:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty q[s(q) - 1]\sin(qr)dq \quad [1]$$

where $\rho(r)$ is the microscopic pair density of Au nanoparticles in this work, and ρ_0 is the average number density in a crystal or aggregate domain. These values are calculated from either an ideal crystal or any model containing particle coordinates in real space:

$$G_{\text{calc}}(r) = \frac{1}{r}\sum_i\sum_j [\delta(r - r_{ij})] - 4\pi\rho_0. \quad [2]$$

where the sum goes over all pairs of AuNP i and j within the model separated by r_{ij}. The scattering patterns of AuNP i and j are the same in this work, and thus are neglected in Eq. **2**. In this figure, the PDF for a perfect HCP crystal is shown in purple, whereas the PDF for a perfect FCC crystal is shown in green. Note the differences between the initial and final scans and their relative correspondence to the perfect FCC and HCP data, particularly the positions of peaks at ≈500 Å and 680–720 Å [Proffen T, Neder RB (1997) DISCUS, a program for diffuse scattering and defect structure simulations. *J Appl Crystallogr* 30:171].

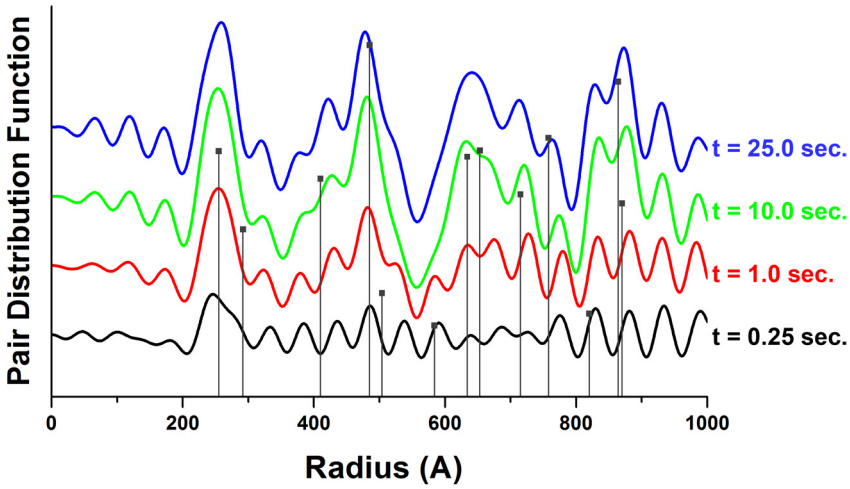

Fig. S6. Pair distribution functions for the 5-nm DNA-AuNP BCC system. In this figure, the PDF for a perfect BCC crystal is shown in gray. Note that the final scan (t = 25.0 s) is more aligned with the predicted BCC pattern than is the initial scan (t = 0.25 s).