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DNA guided crystalline organization of nanoparticles

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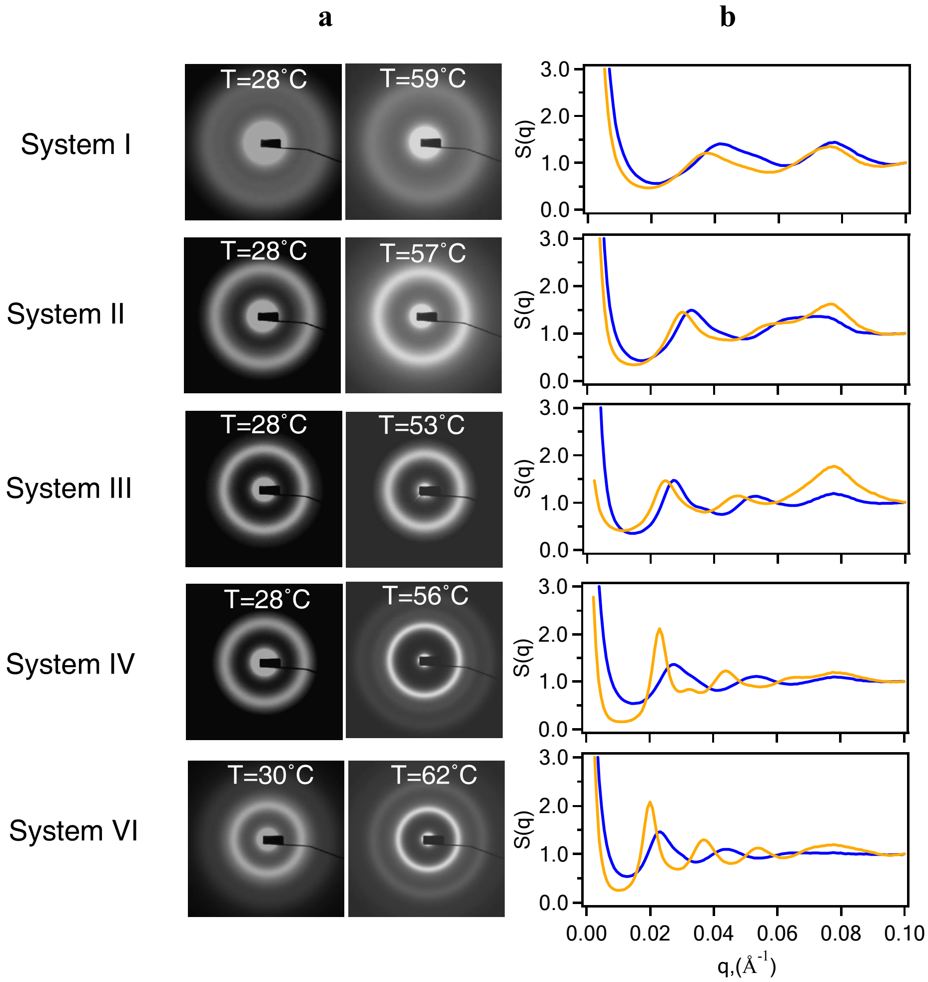
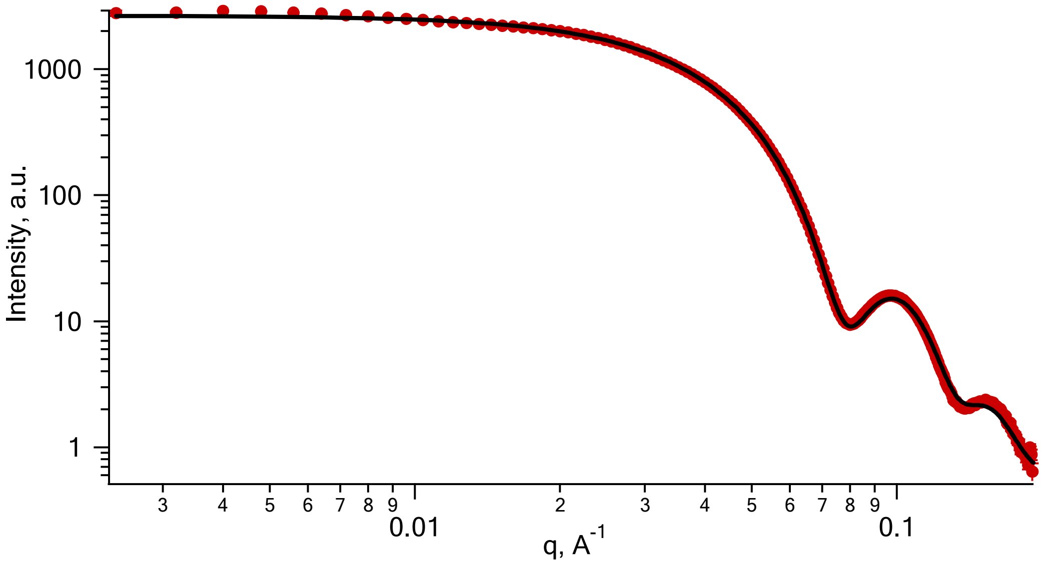
Supplementary Discussion

Thermal behaviour of DNA-nanoparticle systems before annealing: Upon heating the aggregates assembled at room temperature, system I-IV and VI (Table S1), we observed three structurally distinct regimes with SAXS. First, (1) the initially disordered amorphous state at room temperature after assembly (Figure S1a), (2) a structural reorganization due to heating to pre-melting temperatures (T_{pm}) (Figure S1a), and (3) a disassembled state above the DNA linkers melting temperature (T_m). In each system, we observed the shift of S(q) peak to lower q values at higher temperatures, indicating a d expansion with temperature. For example, system IV showed a q-shift of ~0.005A^{-1}, which corresponds to ~20% (~4.5 nm) increase in particle surface-to-surface distance. The larger interparticle distances can be attributed to the development of more uniaxial character of hybridization with annealing, as well as to the conformational changes of DNA with increased temperature.[31] At T_{pm}, SAXS revealed a narrowing of S(q) peak for each system, which is an indication of improved ordering. Compared to room temperature, in systems I, II, and III we observed a 10-20% increase of scattering correlation length, $\xi \approx 2\pi/\Delta q$, where Δq is resolution corrected ($\Delta q_{res} \approx 0.0015$Å^{-1}) FWHM of the diffraction peak. This shows that ξ is limited to only few interparticle spacings, thus still indicating essentially amorphous organization of particles. In contrast, systems IV and VI revealed more than 50% ξ increase, to about $5d$, accompanied by the emergence of higher order peaks, suggesting the presence of relatively ordered domains.



Supplementary Figure S1. SAXS patterns (**a**) and corresponding structure factors S(q) (**b**) for as-assembled systems and annealed at T_{pm}. The experimental temperature indicated on each image. Blue and yellow curves representing S(q) for room and T_{pm} respectively. Positions of the first S(q) peaks are q_{I}=0.0403, q_{II}=0.0324, q_{III}=0.0273, q_{IV}=0.0266, and q_{VI}=0.0226 $Å^{-1}$ at low temperature and q_{I}=0.037, q_{II}=0.0298, q_{III}=0.0244, q_{IV}=0.0233, and q_{VI}=0.0199 $Å^{-1}$ at T_{pm}.



Supplementary Figure S2. Scattering intensity from system IV at 71°C (solid symbols). Solid line represent fitting using spheroidal model for particles with Gaussian size distribution. Fitted particle diameter 11.5±1.2 nm. Fitting performed with Irena 2 macros package (available at http://usaxs.xor.aps.anl.gov/staff/ilavsky/irena.html).

Supplementary Table S1. The ssDNA used in the study

<table>
<tr><th></th><th>DNA Sequence (5’ to 3’)</th></tr>
<tr><td colspan="2"><u>System-I</u></td></tr>
<tr><td>A</td><td>TAC TTC CAA TCC AAT TTT-C_6H_{12}-SH</td></tr>
<tr><td>B</td><td>ATT GGA TTG GAA GTA TTT-C_6H_{12}-SH</td></tr>
<tr><td colspan="2"><u>System-II</u></td></tr>
<tr><td>A</td><td>TAC TTC CAA TCC AAT TTT TTT TTT TTT TTT-C_3H_6-SH</td></tr>
<tr><td>B</td><td>ATT GGA TTG GAA GTA TTT TTT TTT TTT TTT-C_3H_6-SH</td></tr>
<tr><td colspan="2"><u>System-III</u></td></tr>
<tr><td>A</td><td>TAC TTC CAA TCC AATT CTT GTG TC GAT AGG TCG GTT GCT TTT TTT TTT TT-C_6H_{12}-SH</td></tr>
<tr><td>B</td><td>ATT GGA TTG GAA GTA TTT TTT TTT TTT TTT-C_3H_6-SH</td></tr>
<tr><td colspan="2"><u>System-IV</u></td></tr>
<tr><td>A</td><td>TAC TTC CAA TCC AAT TCT TGT GTC GAT AGG TCG GTT GCT TTT TTT TTT TT-C_6H_{12}-SH</td></tr>
<tr><td>B</td><td>ATT GGA TTG GAA GTA TCT TGT GTC GAT AGG TCG GTT GCT TTT TTT TTT TT-C_6H_{12}-SH</td></tr>
<tr><td colspan="2"><u>System-V</u></td></tr>
<tr><td>A</td><td>SH-C_6H_{12}-TTT TTT TTT TTT TTT TTT TTT TTT TTT CGT TGG CTG GAT AGC TGT GTT CTT AAC CTA ACC TTC AT</td></tr>
<tr><td>B</td><td>SH-C_6H_{12}-TTT TTT TTT TTT TTT TTT TTT TTT TTT CGT TGG CTG GAT AGC TGT GTT CTA TGA AGG TTA GGT TA</td></tr>
<tr><td colspan="2"><u>System-VI</u></td></tr>
<tr><td>A</td><td>TAC TTC CAA TCC AAT TCT TGT GTC GAT AGG TCG GTT GCT TTT TTT TTT TT-C_6H_{12}-SH
||| ||| ||| ||| ||| ||| ||| ||| ||| ||| ||| ||
3’-AGA ACA CAG CTA TCC AGC CAA CGA AAA AAA AAA AA-5’</td></tr>
<tr><td>B</td><td>ATT GGA TTG GAA GTA TCT TGT GTC GAT AGG TCG GTT GCT TTT TTT TTT TT-C_6H_{12}-SH
||| ||| ||| ||| ||| ||| ||| ||| ||| ||| ||| ||
3’-AGA ACA CAG CTA TCC AGC CAA CGA AAA AAA AAA AA-5’</td></tr>
</table>

Supplementary Table S2: Results of UV-vis melting analysis for assembled aggregates.

	Melting Analysis
System	T_m (°C)
I	63.4 (±0.5)
II	64.0 (±0.5)
III	64.3 (±0.6)
IV	63.1 (±0.3)
V	62.5(±0.3)
VI	66.3 (±0.5)

Supplementary Table S3. Interparticle spacing *d* obtained from the first scattering peak of SAXS data and worm-like chain model[32] idealized estimates d_w, for aggregates assembled at room temperature.

System	d, (nm)	d_w, (nm)
I	15.6	17.8
II	19.4	19.9
III	23	21.3
IV	23.6	22.5
V	-	24.2
VI	27.8	37.8

SupplementaryNotes

31. Zhou, J., Gregurick, S. K., Krueger, S. & Schwarz, F. P. Conformational changes in single-strand DNA as a function of temperature by SANS. *Biophys. J.* **90**, 544-551 (2006).

32. Rivetti, C., Walker, C. & Bustamante, C. Polymer chain statistics and conformational analysis of DNA molecules with bends or sections of different flexibility. *J. Mol. Biol.* **280**, 41-59 (1998).