Supplementary Information

Optimizing the dynamic and thermodynamic properties of hybridization in DNA-mediated nanoparticle self-assembly

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Calculation method of related physical quantities

1. Distance between two paired sticky beads

As strand-to-strand separation of DNA duplex is about σ (**Fig. S1**), the distance of about σ between two sticky beads is reasonable for forming a hydrogen bond. Therefore, DNA hybridization or duplex formation herein is defined if a sticky bead of a DNA strand is within the distance of σ away from its complementary sticky bead, namely, forming a hydrogen bond.
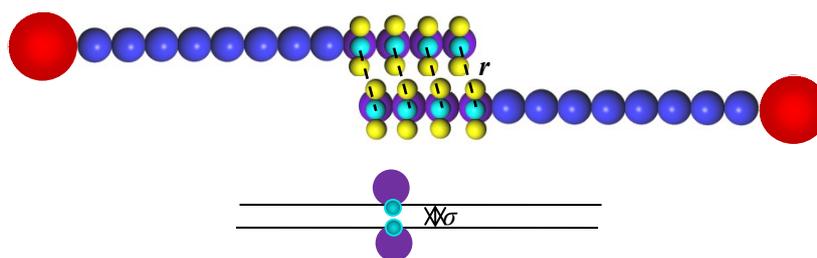

Fig. S1 Example of hybridization between two DNA-NPs by linker-linker pairing interaction. The distance between two paired sticky beads $r = \sigma$.

2. Determine BCC lattice by structure factor

The structure factor is defined as $S(\vec{q}) = \frac{1}{N}\left\langle \sum_{jk} e^{-i\vec{q}\cdot(\vec{r_j}-\vec{r_k})} \right\rangle$, where $\vec{q}$ is the wave vector, N is the number of nanoparticles, $\vec{r_j}, \vec{r_k}$ ($j, k = 1, 2, 3, ... N$) are the positions of NPs.[1,2] For BCC, the peaks q_1, q_2, q_3, q_4, q_5, q_6, q_7, q_8 is equal to $\sqrt{2}, \sqrt{4}, \sqrt{6}, \sqrt{8}, \sqrt{10}, \sqrt{12}, \sqrt{14}, \sqrt{16}$ corresponding to crystallographic planes (101), (200), (211), (220), (301), (222), (321), (400) (**Fig. S2**). Our simulation result agrees well with the theoretical peaks.
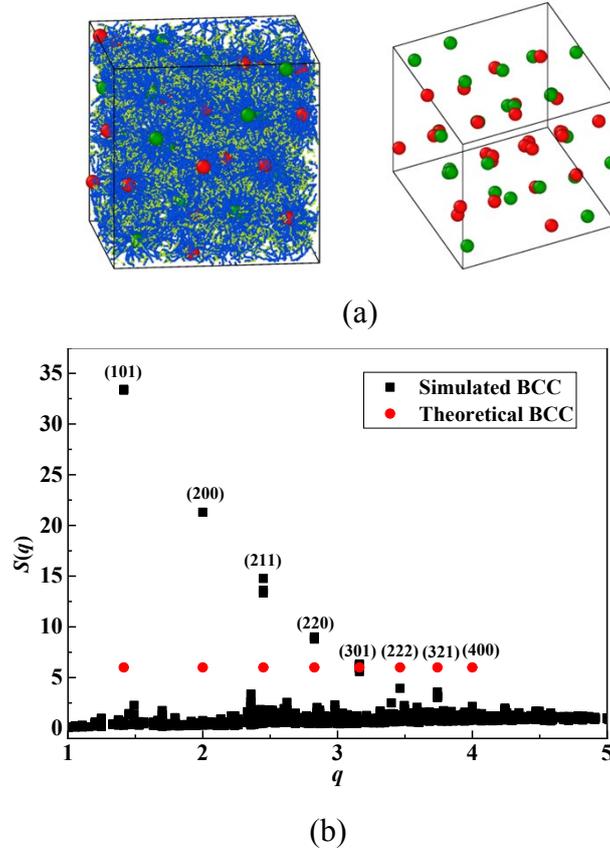

(a)

(b)

Fig. S2 (a) BCC lattice snapshot (left: all DNA-NP beads, right: only nanoparticle beads) obtained from MD simulation under the conditions $n_l = 3$, $n_s = 8$, $n = 50$, $D = 10$ at $T = 1.4$. (b) Structure factor is used to determine the lattice structure.

3. Average distance between hybrid nearest neighbor A and B nanoparticles r_0

The nearest neighbor distance r_0 between hybrid nearest-neighbor A and B nanoparticles present an increasing trend due to increasing nanoparticle size D (**Fig. S3a**). r_0 can be identified by the first sharp peak position of pair radial distribution function $g(r)$ (**Fig. S3b**), giving the probability

of finding a particle (or molecule) at distance r away from a reference particle, relative to that for the ideal gas distribution.[3] Although, $g(r)$ can be measured for separations no greater than one half the edge length of the simulation cell ($L = L_x = L_y = L_z$), the first peak position r_0 ($r_0 < L/2$) is indeed reliable. More importantly, the number integral over $g(r)$ for the first peak square corresponds to coordination number ($N_{coor} = 2\int_0^{r_0} 4\pi r^2 \rho_0 g(r)\mathrm{d}r$, ρ_0 is the average number density) of nanoparticles, saying the average number of hybrid nearest-neighbor A and B nanoparticles.[4, 5] **Fig. S3c** shows coordination number presents a downward trend with increasing nanoparticle size D.
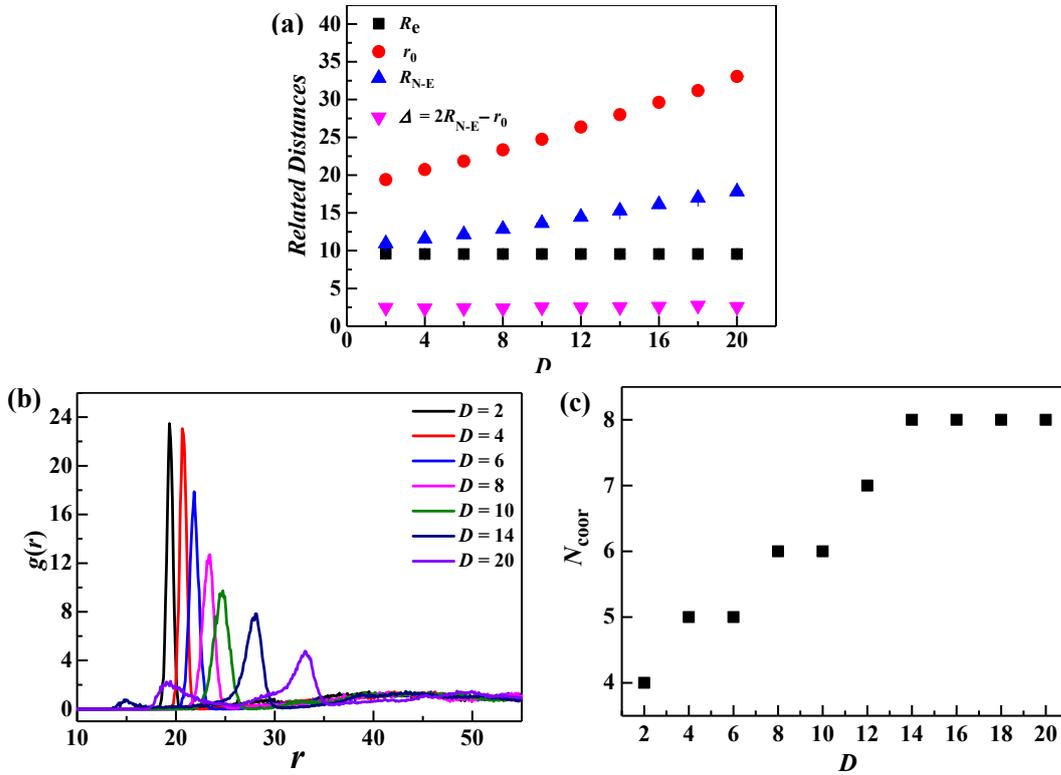

Fig. S3 (a) Related distances containing R_e, r_0, R_{N-E} and Δ as a function of nanoparticle size D in DNA-NP systems with $D = 2\sim20$, $n = 60$, $n_l = 3$ and $n_s = 8$ at $T = 1.3$. Here R_e, r_0, R_{N-E} represent the root mean square end-to-end distance of DNA chains, average distance between hybrid nearest-neighbor A and B nanoparticles, average distance between nanoparticles and the end of DNA chains, respectively. $\Delta = 2R_{N-E}-r_0$, representing contact distance parameter of sticky linker beads. (b) Radical distribution functions $g(r)$ of nanoparticles. (c) Coordination number ($N_{coor} = 2\int_0^{r_0} 4\pi r^2 \rho_0 g(r)\mathrm{d}r$, ρ_0 is the average number density) of nanoparticles, namely, the average number of hybrid nearest-neighbor A and B nanoparticles.

4. Effective volume fraction ϕ

If every DNA-NP molecule is regarded as a sphere, the volume fraction of all DNA-NP spheres is calculated by $\phi_0 = \dfrac{4\pi N R_{\text{N-E}}^3}{3L^3}$ where $R_{\text{N-E}}$ is the average distance between nanoparticle and the end of DNA chains, N (= 54) is the number of nanoparticles in our simulation system, L is the length of simulation box length. Thus, the volume V_h of hybrid shadow part is double-counted and should be subtracted (**Fig. S4a**).

The shadow part volume $V_h = 2\pi H^2 (R - H/3)$, where R is the radius of the sphere, H is the height of the spherical cap in **Fig. S4b**. Here $R = R_{\text{N-E}}$, $H = \Delta/2 = R_{\text{N-E}} - r_0/2$, then $V_h = \dfrac{4}{3}\pi R_{\text{N-E}}^3 - \pi R_{\text{N-E}}^2 r_0 + \dfrac{\pi}{12} r_0^3$. There is not only one nanoparticle to bond with every nanoparticle by DNA interaction in the DNA-NP systems. We estimate volume fraction of all hybrid parts $f_h = N_{\text{coor}} V_s / (\dfrac{4}{3}\pi R_{\text{N-E}}^3)$, then $f_h = [1 - \dfrac{3}{4}\dfrac{r_0}{R_{\text{N-E}}} + \dfrac{1}{16}(\dfrac{r_0}{R_{\text{N-E}}})^3] N_{\text{coor}}$ where N_{coor} is the number of nearest neighbor nanoparticles, saying the number of hybrid parts. Therefore, The real effective volume fraction $\phi = \dfrac{4\pi N R_{\text{N-E}}^3}{3L^3}(1 - f_h)$.
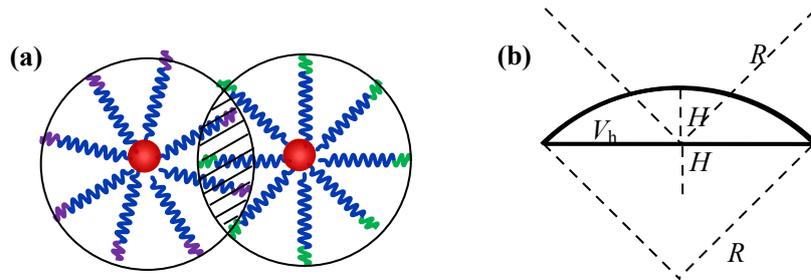

Fig. S4 (a) Schematic illustration of hybridization between two DNA-NPs by linker-linker pairing interaction for binary self-assembly system. (b) Sketch drawing of the shadow part.

5. Free energy calculated by nearest-neighbor rule

Herein, we take the base sequences 5'TAAT TAAT TAAT-3'/3'-ATTA ATTA ATTA-5' as an example to calculate the free energy by using the nearest-neighbor rule[6, 7]:

$\Delta G°_{37}(\text{total}) = \Delta G°_{37 \text{ initiation}} + \Delta G°_{37 \text{ symmetry}} + \Sigma \Delta G°_{37 \text{ stack}} + \Delta G°_{\text{AT terminal}}$

5'-TAAT TAAT TAAT-3' $= \Delta G°_{37 \text{ initiation}} + \Delta G°_{37 \text{ symmetry}} + 2(\text{TA} + \text{AA} + \text{AT} + \text{TT}) + \text{TA} + \text{AA} + \text{AT} + \text{AT}_{\text{ terminal}}$

3'-ATTA ATTA ATTA-5'   AT   TT   TA   AA   AT   TT   TA

$\Delta G°_{37}(\text{predicted}) = 1.96 + 0 + 2 \times (-0.58 - 1.00 - 0.88 - 1.00) - 0.58 - 1.00 - 0.88 + 0.05$

$= -7.37 \text{kcal/mol} = -30.84 \text{kJ/mol}$

Table S1. Nearest-neighbor thermodynamic parameters for DNA Watson-Crick pairs in 1 M NaCl[7]

Propagation sequence	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (e.u.)	$\Delta G°$ (kcal mol^{-1})
AA/TT	-7.6	-21.3	-1.00
AT/TA	-7.2	-20.4	-0.88
TA/AT	-7.2	-21.3	-0.58
CA/GT	-8.5	-22.7	-1.45
GT/CA	-8.4	-22.4	-1.44
CT/GA	-7.8	-21.0	-1.28
GA/CT	-8.2	-22.2	-1.30
CG/GC	-10.6	-27.2	-2.17
GC/CG	-9.8	-24.4	-2.24
GG/CC	-8.0	-19.9	-1.84
Initiation	+0.2	-5.7	+1.96
Terminal AT penalty	+2.2	+6.9	+0.05
Symmetry correction	0.0	-1.4	+0.43

The slash indicates the sequences are given in antiparallel orientation. (e.g., AC/TG means 5'-AC-3' is Watson-Crick base paired with 3'-TG-5'). The symmetry correction applies to only self-complementary duplexes. The terminal AT penalty is applied for each end of a duplex that has a terminal AT (a duplex with both end closed by AT pairs would have a penalty of +0.1 kcal/mol for $\Delta G°_{37}$). 1 kcal/mol = 4.184 kJ/mol.
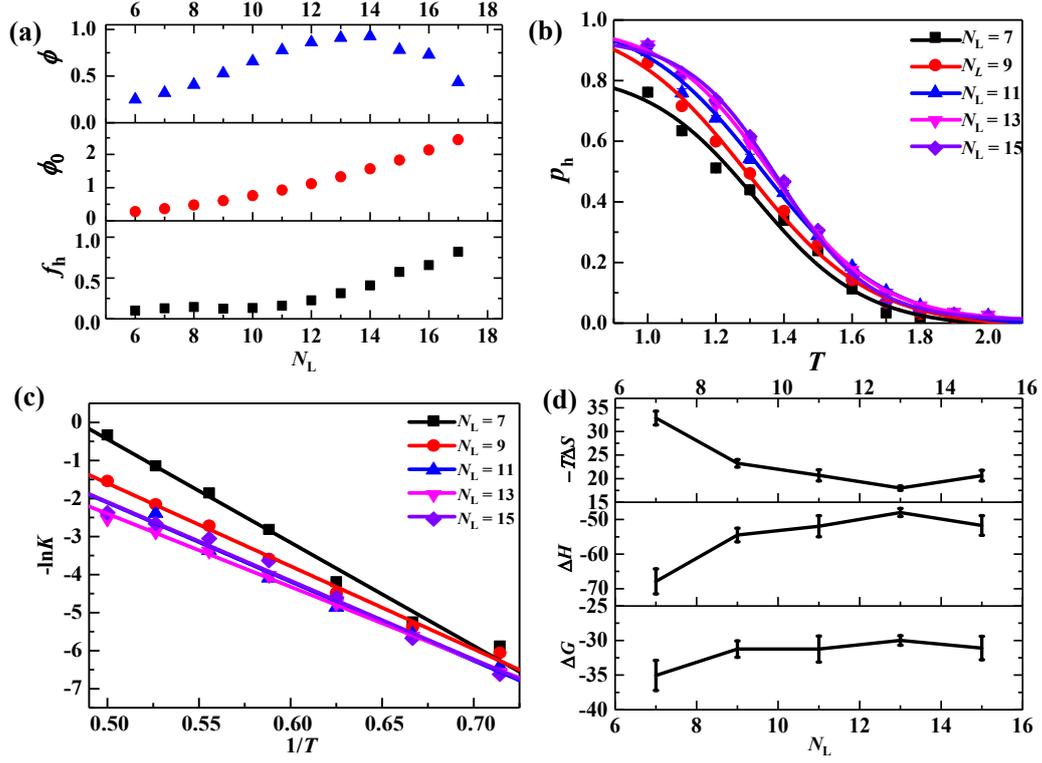
Fig. S5 Hybridization properties for DNA-NP systems with DNA chain length $N_L = 6\sim17$, $n_l = 3$, $D = 10$, $n = 60$. (a) The three panels represent the volume fraction of all hybrid parts f_h, volume fraction of all DNA-NP spheres ϕ_0 and real effective volume fraction $\phi = \phi_0(1-f_h)$ at $T = 1.3$, respectively. (b) p_h as a function of T. (c) -ln$K$ as a function of $1/T$: the solid lines are least-square fits to the data points from simulation. (d) ΔG, ΔH and $-T\Delta S$ in unit of kJ/mol of DNA hybridization as a function of N_L at room temperature.
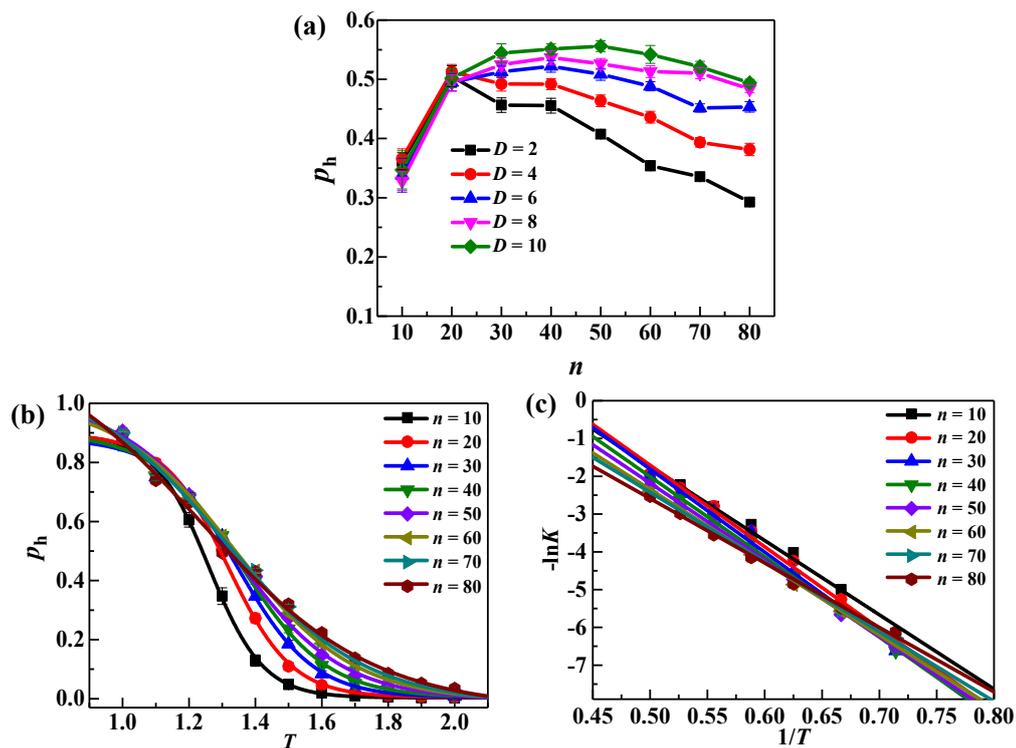
Fig. S6 Hybridization properties for DNA-NP systems with different number of DNA chains ($n = 10\sim80$) grafted on one nanoparticle, $D = 2\sim10$, $n_l = 3$ and $n_s = 8$. (a) p_h as a function of chain number n for DNA-NP systems with $D = 2\sim10$. (b) p_h as a function of T for $n = 10\sim80$, $D = 10$. (c) -ln$K$ as a function of $1/T$: the solid lines are least-square fits to the data points from simulation.
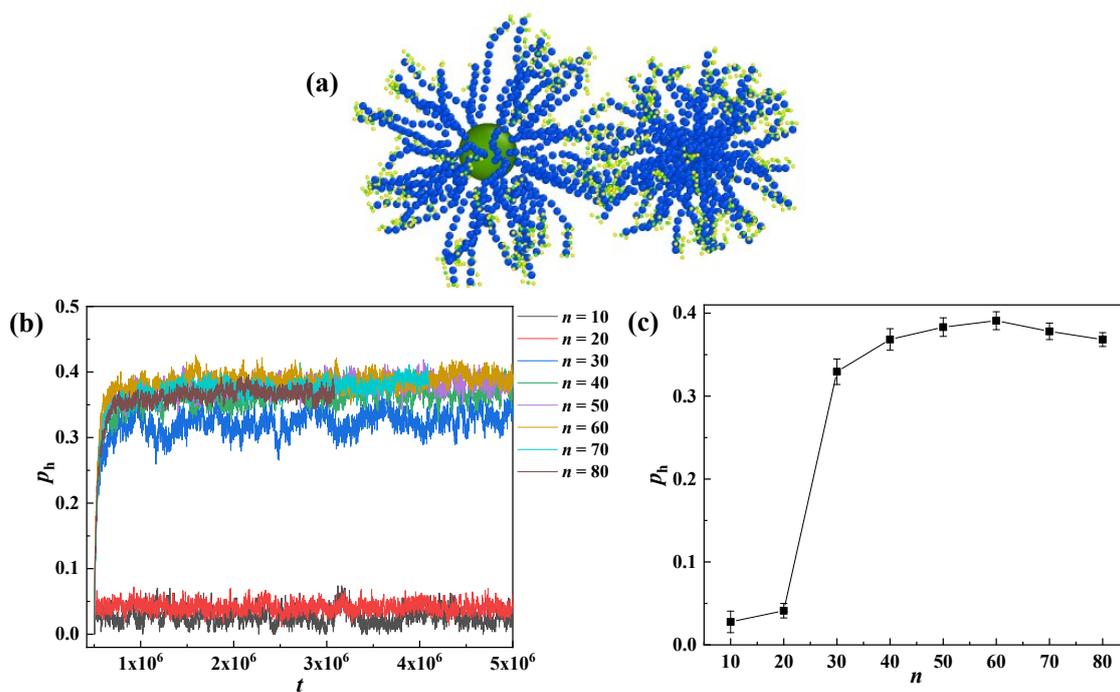
Fig. S7 (a) Hybridization example of two DNA-NPs with different nanoparticle sizes. (b) Hybridization percentage p_h as a function of simulation step time t for DNA-NP systems with different chain number $n = 10\sim80$, $n_l = 3$ and $n_s = 8$ at $T = 1.3$. (c) Average hybridization percentage p_h as a function of n.

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