

Supplementary Information

Significance of the DNA bond strength in programmable nanoparticle thermodynamics and dynamics

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Model and Methods

Force field. In the coarse-grained model, the DNA backbone beads have a diameter of σ , and the nanoparticles (NPs) 6σ . The protection and sticky beads attached to linker beads both have a diameter of 0.6σ . Any two neighboring beads i and j of a DNA are covalently bonded via the potential

$$V_{\text{bond}}(r) = \frac{1}{2}k_s(r - r_0)^2 \quad (\text{S1})$$

where the strength $k_s = 330 \text{ } \varepsilon/\sigma^2$ and preferred length $r_0 = 0.84 (R_i + R_j)$ with R_i and R_j the beads' radii. The DNA chain is stiffened by the angular potential

$$V_{\text{angle}}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \quad (\text{S2})$$

which acts on three consecutive beads. The strength $k_\theta = 100 k_B T/\text{rad}^2$ and the angle θ assumes the preferred value $\theta_0 = \pi$. The same potential is applied to the three additional beads attached to each linker bead. The excluded-volume interaction between any nonbonded pair of beads i and j (except for the complementary pairs of two DNA) is modeled by the Weeks-Chandler-Andersen (WCA) potential

$$U(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma_{\text{WCA}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{WCA}}}{r}\right)^6\right] + \varepsilon, & r \leq r_c \\ \mathbf{0}, & r > r_c \end{cases} \quad (\text{S3})$$

where ε is the strength, $\sigma_{\text{WCA}} = R_i + R_j$ and the cutoff $r_c = 2^{1/6}\sigma_{\text{WCA}}$. The interaction between complementary sticky beads of two DNA chains takes the form

$$U_{\text{LJ}}(r) = \begin{cases} 4\varepsilon_{\text{LJ}}\left[\left(\frac{\sigma_{\text{LJ}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r}\right)^6\right] + 0.0163\varepsilon_{\text{LJ}}, & r \leq r_c \\ \mathbf{0}, & r > r_c \end{cases} \quad (\text{S4})$$

with $\sigma_{\text{LJ}} = \sigma$, and $r_c = 2.5\sigma$. We assume the WCA potential strength ε is independent of temperature and $\varepsilon = k_B T_0 = 2.48 \text{ kJ mol}^{-1}$ for $T_0 = 298 \text{ K}$. To ensure efficient sampling in our simulations, we choose $\varepsilon_{\text{LJ}} = 10\varepsilon = 24.8 \text{ kJ mol}^{-1}$ smaller than the experimental A-T and C-G bond enthalpy of -49.4 and $-99.6 \text{ kJ mol}^{-1}$ at 298 K . Therefore, one coarse-grained linker bead represents a 'ATAT' or 'TATA' rather than 'CGCG' or 'GCGC' sequence.

MD simulations. We simulate both DNA-NP and DNA systems at the temperature range of $1.0\text{--}2.2 \varepsilon/k_B$ in a cubic box of size $V = (60\sigma)^3$ with periodic boundaries. For simplicity, all beads are assumed to have equal mass, $m = 1$. A relaxation run of $(2\text{--}3)\times 10^3 t_0$ is performed for thermal equilibration in each system before the production run of $(0.5\text{--}2)\times 10^5 t_0$ for statistical sampling. We estimate the physical time scale by comparing simulation results with the experimental lifetimes of a A-T or C-G pair. Fitting the data points in **Fig. 3(a)** to the Arrhenius equation $k_{\text{off}} = A \exp(-E_a/k_B T)$ yields the prefactor A and activation energy E_a at different number of A-T base pairs as shown in **Fig. S2**. Combination of the prefactor extrapolated to one base pair with the activation energy of 2ε per base pair leads to the mean lifetime of $2.4t_0$. In a series of 20 B-DNA duplexes experiment²⁻⁴, the A-T and C-G base pair lifetimes are in the range of $0.7\text{--}7$ ms and $5\text{--}50$ ms at 15°C , respectively. Letting $2.4t_0 \approx 1$ ms, we obtain the physical time scale $t_0 \approx 0.4\text{ms}$.

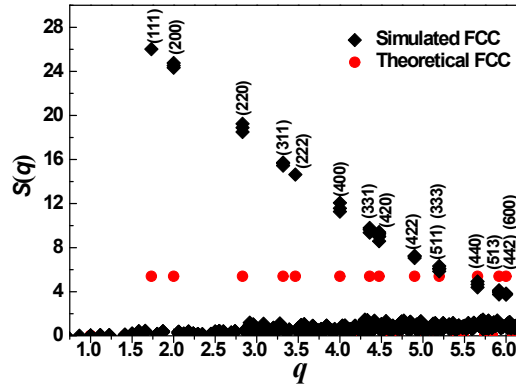


Fig. S1. Static structure factor $S(q)$ for FCC at $n_1 = 4$, $n_s = 7$, $T = 1.45 \varepsilon/k_B$. The structure

factor is defined as $S(\mathbf{q}) = \frac{1}{N} \left\langle \sum_{jk} e^{-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} \right\rangle$, where \mathbf{q} is the wave vector, N is the

number of NPs, $\mathbf{r}_j, \mathbf{r}_k$ ($j, k = 1, 2, 3, \dots, N$) are the positions of NPs.⁵

T_m determined by Lindemann melting rule

The Lindemann melting rule indicates that fusion occurs when the ratio ΔL of the root mean square fluctuation ($RMSF$) of atomic positions about the equilibrium lattice positions and the nearest neighbor distance r_0 , exceeds a critical value.⁶

$$\Delta L = RMSF / r_0 \quad (\text{S5})$$

$$RMSF \equiv \sqrt{\frac{1}{N_t} \sum_{t=1}^{N_t} (x_t - \bar{x}_0)^2} \quad (\text{S6})$$

Where N_t is the number of timepoints over which one particle wants to average, x_t is the position at t timepoint, and \bar{x}_0 is the time-averaged position of the same particle. r_0 is the first sharp peak position of pair radial distribution function $g(r)$ (**Fig. S2(a)**), 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. Although, $g(r)$ can be measured for separations no greater than one half the edge length of the simulation cell ($L = L_x = L_y = L_z = 60.0\sigma$), the first peak position r_0 ($r_0 < L/2$) is indeed reliable. The threshold value of ΔL may vary between 5% and 20% depending on the crystal structure, nature of interparticle interactions, and magnitude of quantum effects.⁶ For T_m obtained from the above hybridization, the corresponding $RMSF$ and ΔL value is close to 1.0, 5%, respectively (**Fig. S2(b)**), in the range of threshold value of ΔL . Supposing DNA-NP self-complementary system melts when the ΔL reaches 5%, we can evaluate corresponding T_m in the range of error permitted, in accord with T_m obtained from the melting curve p_h versus T (**Table 1**). This Lindemann rule allows one to predict the melting temperature T_m on the basis of solid state properties.

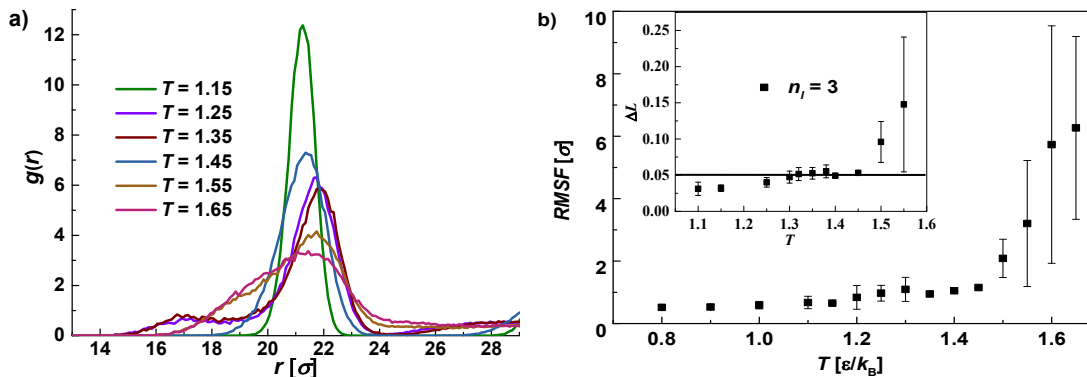


Fig. S2. (a) Radial distribution function $g(r)$ at different temperatures; (b) Root mean square fluctuation ($RMSF$) and Lindemann parameters ΔL (**Inset**) as the function of temperature T . Supposing DNA-NP system melts when the Lindemann parameter ΔL is equal to 5%, the T_m as following: $n_l = 3$, $n_s = 8$, $T_m = 1.32 \pm 0.02$, in agreement with T_m obtained from the melting curve p_h versus T , providing a new pathway for DNA-NP system to characterization analysis of T_m .

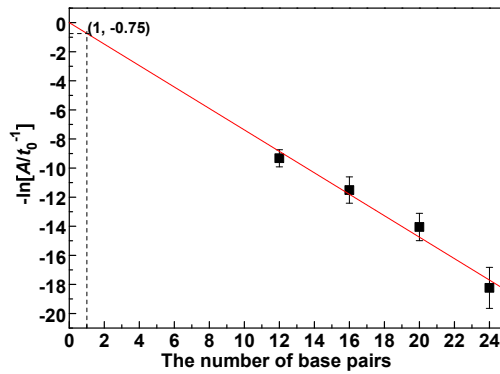


Fig. S3. The prefactor A of the Arrhenius equation $k_{\text{off}} = A \exp(-E_a/k_B T)$ at different number of A-T base pairs obtained from fitting the data points in **Fig. 3(a)**. The linear extrapolation given by the solid red line for one A-T base pair gives $A = e^{0.75} t_0^{-1}$.

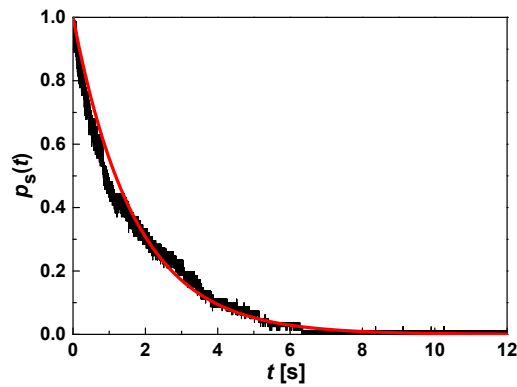


Fig. S4. The survival percentage of DNA duplexes obtained from simulations with $n_l = 4$, $n_s = 7$, $T = 1.3 \epsilon/k_B$. The initial number of duplexes is $n_0 = 81$. The simulation data can be well fitted to the solid red line given by $p_s(t) = \exp(-n_0 k_{\text{off}} t)$ with $k_{\text{off}} = 7.5 \times 10^{-3} \text{ s}^{-1}$.

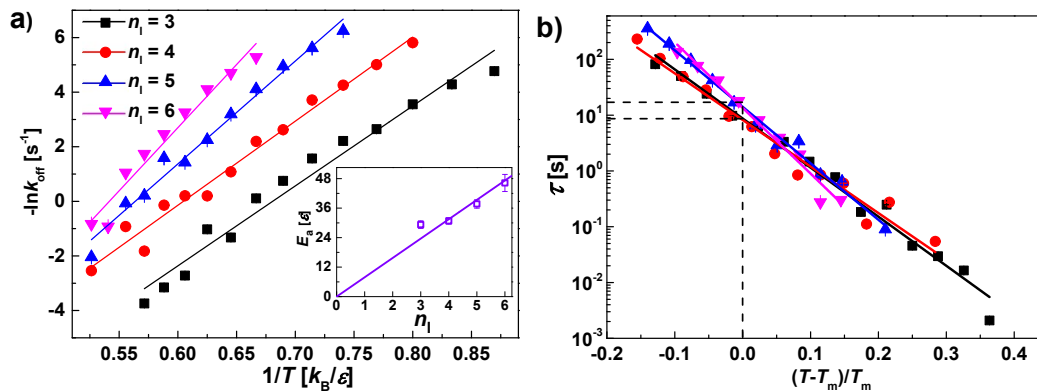


Fig. S5. Dehybridization kinetics of DNA duplexes in pure DNA systems with fixed DNA length $n_s + n_l = 11$. (a) Dehybridization rate constant k_{off} vs. inverse temperature. Insert: Activation energy of dehybridization vs. linker bead number n_l . (b) Mean lifetime of DNA duplexes vs. relative temperature. The solid lines are least-square fits to the data points. The dash-dotted line indicates the lifetime at melting temperature.

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