

Supporting information:

Mechanism of DNA Assembly as Revealed by Energy Barriers

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Experimental Section

Materials.

The 52-base-long, single strand DNA tiles were purchased from Invitrogen Corporation (Shanghai, China) and used as received. Tris base (tris(hydroxymethyl)aminomethane) and EDTA (ethylenediamine tetraacetic acid) were purchased from Sigma-Aldrich Co., LTD. Acetic acid and magnesium acetate [Mg(Ac)₂] were purchased from Beijing Chemical Reagent Company. TAE/Mg²⁺ buffer consisting of Tris base (40 mM), acetic acid (20 mM), EDTA (2 mM), and Mg(Ac)₂ (12.5 mM) were prepared by Milli-Q water. DNA tiles at 3 μM in TAE/Mg²⁺ was used for the assembly. DNA solution was filtered through a 0.45 μm PES filter (Sartorius stedim biotech corp., Germany) and collected in a dust-free sample vial before the measurement.

Laser Light Scattering Measurements.

Static light scattering (SLS) and dynamic light scattering (DLS) experiments are conducted on a commercialized spectrometer (Brookhaven Inc, Holtsville, NY) equipped with a BI-200SM Goniometer and a BI-TurboCorr Digital Correlator. A solid-state laser polarized at the vertical direction (GXL-III, 100mW, CNI, Changchun, China) operating at 633 nm was used as the light source. SLS measurements were carried out at scattering angles in the range of 20°-120°. The time averaged excess scattered intensity at angle θ , also known as the Rayleigh ratio $R_{v,}(\mathbf{q})$, was related with the weight-averaged molar mass M_w , the Z-averaged root mean square radius R_g , the second virial coefficient A_2 , and the scattering vector \mathbf{q} as,

$$\frac{KC}{R_{v,}(\mathbf{q})} \approx \frac{1}{M_w} \left(1 + \frac{1}{3} R_g^2 q^2 \right) + 2A_2 C \quad (1)$$

where $K = 4\pi^2 n^2 (dn/dC)^2 / (N_A \lambda_0^4)$ and $q = (4\pi n / \lambda) \sin(\theta/2)$, with N_A , n , (dn/dC) and λ_0 being the Avagadro constant, the refractive index of the solvent, the specific refractive index increment of the solution, and the wavelength of light in vacuum, respectively.

For DLS, the intensity-intensity time autocorrelation function $G^{(2)}(t)$ was measured in the self-beating mode. It is related to the normalized first order electric field time correlation function $g^{(1)}(t)$ as

$$G^{(2)}(t) = \langle I(0)I(t) \rangle = A \left[1 + \beta |g^{(1)}(t)|^2 \right] \quad (2)$$

where A is the measured base line, β is a coherence factor, t is the delay time, and $g^{(1)}(t)$ is the normalized first-order electric field time correlation function. The line width distribution $G(\Gamma)$ was analyzed with a Laplace inversion program, CONTIN, based on the following relation,

$$g^{(1)}(t) = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \quad (3)$$

The average line width, $\bar{\Gamma}$, was calculated according to

$$\bar{\Gamma} = \int \Gamma G(\Gamma) d\Gamma \quad (4)$$

From the average line width $\bar{\Gamma}$, the average diffusion coefficient D can be calculated as $D = \bar{\Gamma} / q^2$, which was then converted into the hydrodynamic radius R_h by using the Stokes-Einstein equation:

$$R_h = k_B T / 6\pi\eta D \quad (5)$$

Energy Calculation

The energy barrier is calculated from Arrhenius equation:

$$k = A e^{-E_a / RT} \quad (6)$$

with A, E_a , R, and T being the frequency factor, the apparent activation energy, the universal gas constant, and temperature, respectively. The reaction rate k is inversely proportional to the delay time τ_0 , then

$$\ln(1 / \tau_0) = \ln A - E_a / RT \quad (7)$$

The energy barrier E_a and the frequency factor A of the nucleation process can be calculated from the slope and the intercept, respectively. According to transition state theory²,

$$E_a = RT + \Delta_r^+ H_m^\theta \quad (8)$$

with $\Delta_r^+ H_m^\theta$ being the standard molar enthalpy of activation.

The frequency factor A has a positive relationship with $\Delta_r^+ S_m^\theta$, the standard molar entropy of activation,

$$A = \frac{k_B T}{h} e^n (c^\theta)^{1-n} \exp\left[\frac{\Delta_r^+ S_m^\theta (c^\theta)}{R}\right] \quad (9)$$

with k_B , h being Boltzmann constant and Planck constant, respectively.

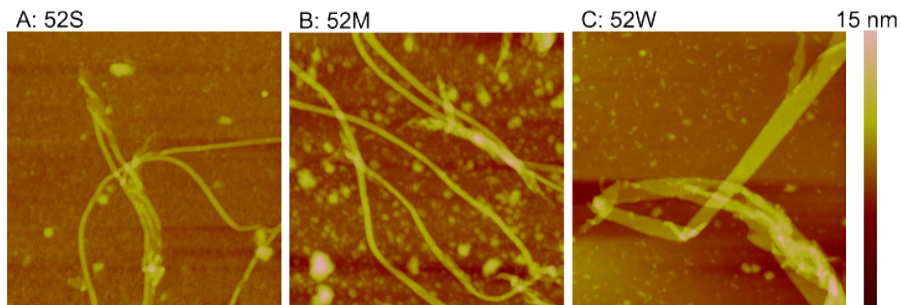


Figure S1. Atomic force microscope (AFM) images of the assembled DNA crystalline structures. The DNA samples (1.0 μM) are annealed from 95 $^\circ\text{C}$ to room temperature. The length of each frame is 3 μm .

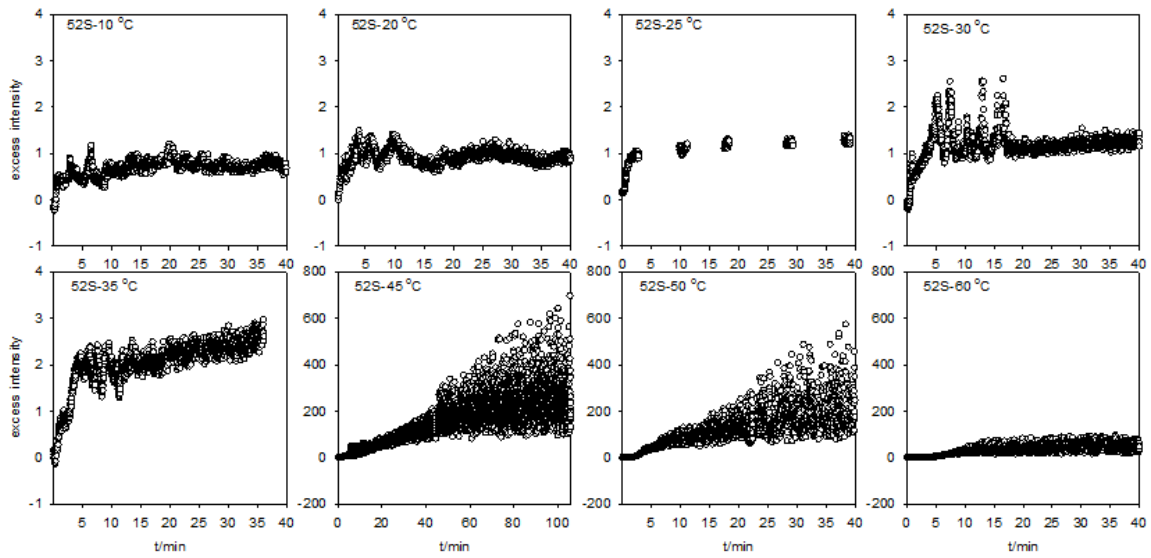


Figure S2. Excess scattered intensity curves of 52S at 30 ° at constant temperatures.

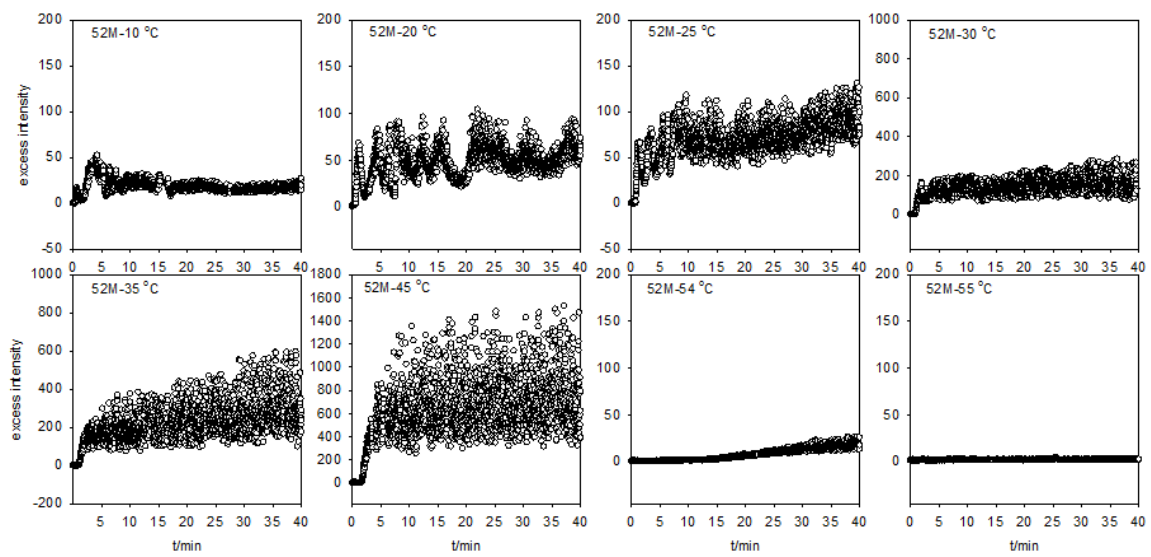


Figure S3. Excess scattered intensity curves of 52M at 30 ° at constant temperatures.

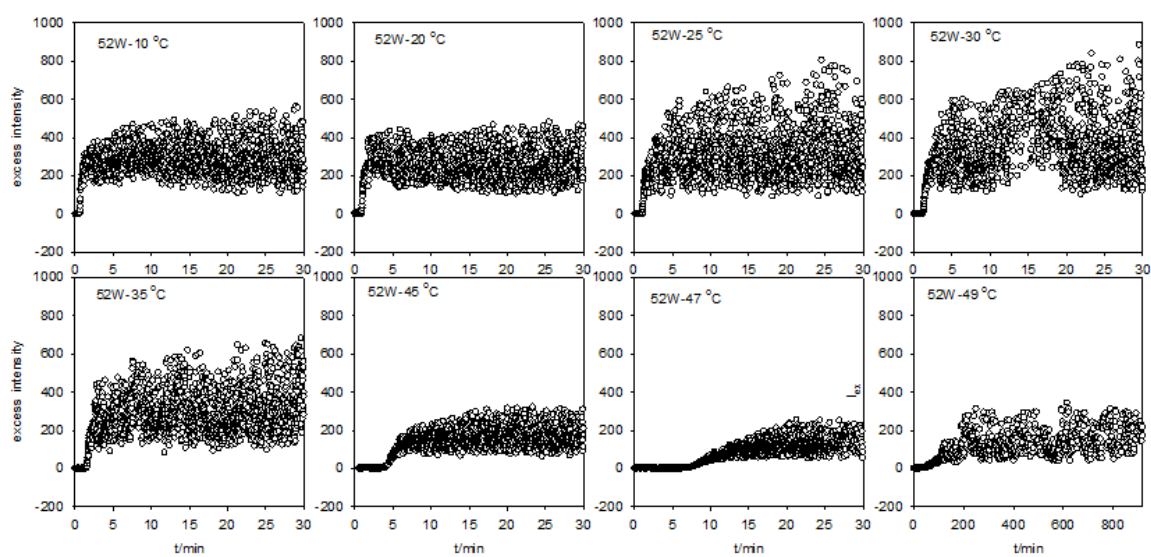


Figure S4. Excess scattered intensity curves of 52W at 30 ° at constant temperatures.

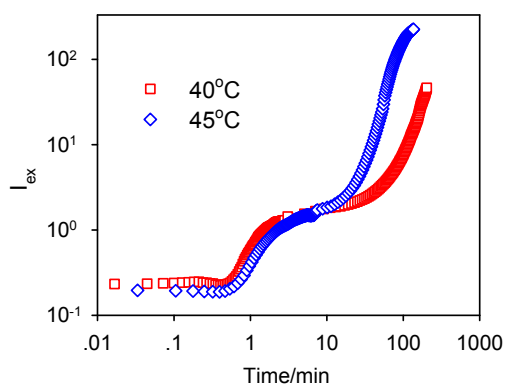


Figure S5: Smoothed scattered intensity of 52S at 2 uM at 40 °C and 45 °C.

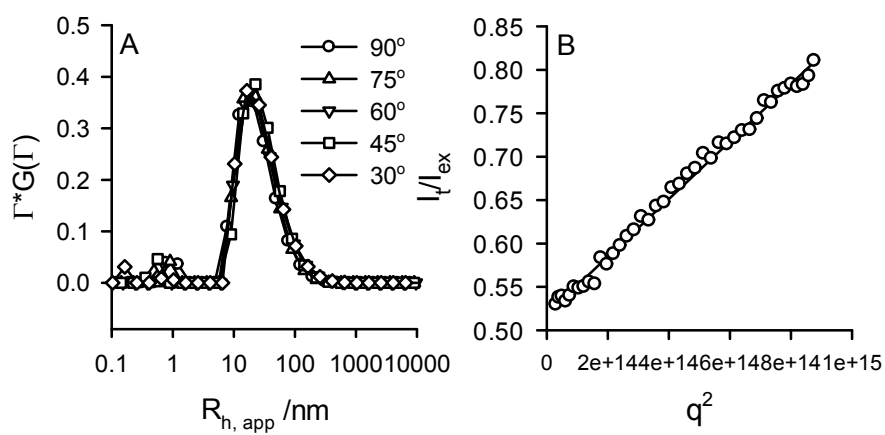


Figure S6. R_h distribution (A) and the angular dependence of the excess scattered intensity (B) of 52S at 25 °C after incubated for 1 hour.

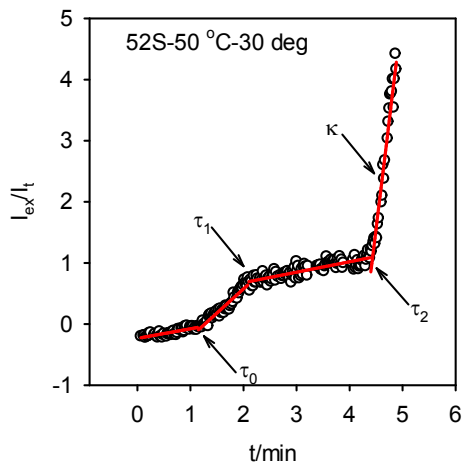


Figure S7. Definition of the parameters used to calculate energy barrier. (52S at 50 °C as an example).

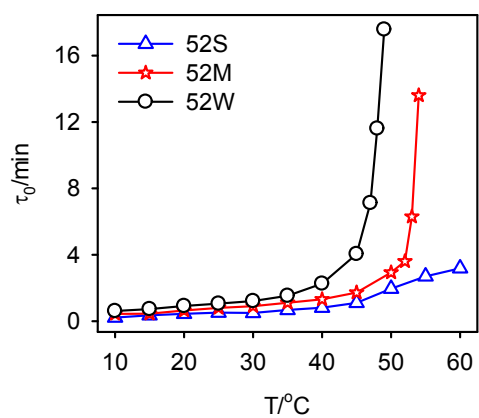


Figure S8. Temperature dependence of τ_0 for the DNA tiles.

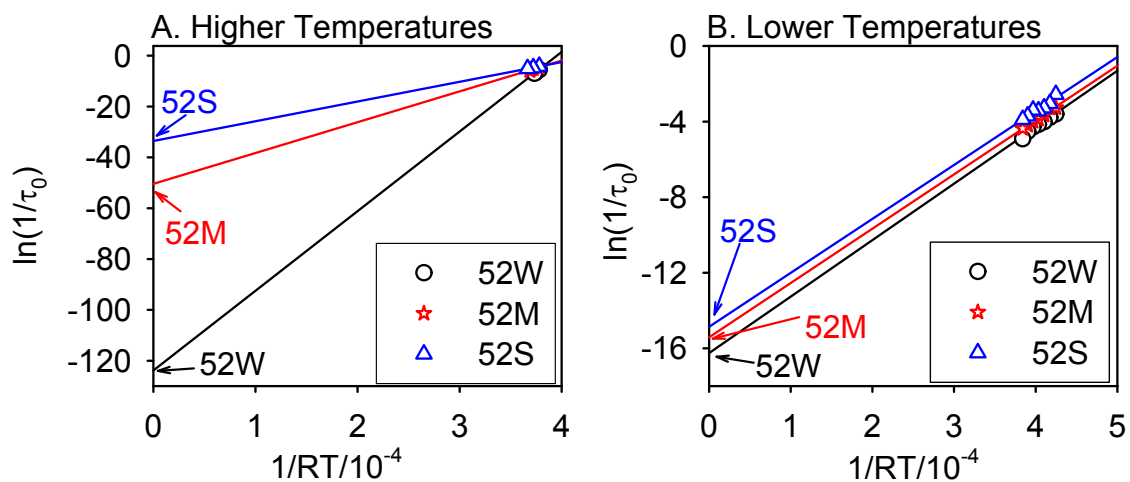


Figure S9. Extrapolated curve to calculate assembly entropy based on transition state theory and Arrhenius equation at higher temperature (A), and lower temperature (B).

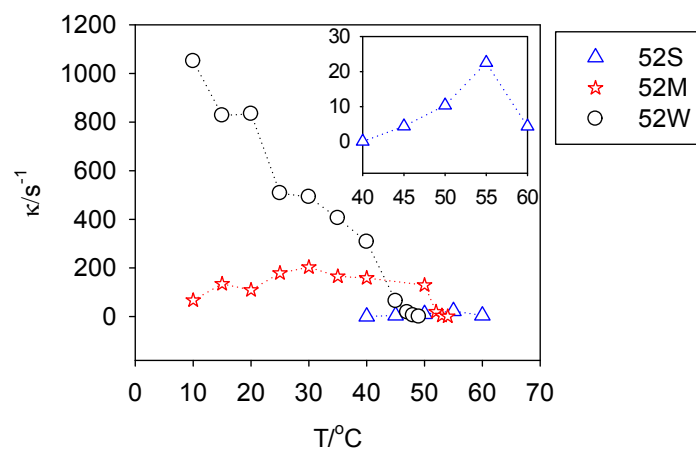


Figure S10. Temperature dependence of the growth rate κ for the three DNA tiles.

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1. J. Zhang, D. Li, G. Liu, K. J. Glover and T. B. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 15152-15159.
 2. D. G. Truhlar, B. C. Garrett and S. J. Klippenstein, *J. Phys. Chem.*, 1996, **100**, 12771-12800.