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Supplementary Materials for

Linker-mediated self-assembly of mobile DNA-coated colloids

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This PDF file includes:

S1: DERIVATION OF COMBINATIONAL TERM $W(\{m_i, q_{ij}\})$ (EQ. 2)

Here we use the mathematical induction method to derive Eq. 2. We start from a configuration in which bridges are formed only between particle 1 and 2 consisting of m_1 and m_2 bonded linkers with free ends on each particle and q_{12} bridging linkers between the two particles (Fig S1a), the number of possible combinations of hybridization, W_2, can be written as:

$$\begin{aligned} W_2 =& \binom{n_1}{m_1}\binom{n_1-m_1}{q_{12}}\binom{n_2}{m_2}\binom{n_2-m_2}{q_{12}} q_{12}! \\ =& \frac{n_1! n_2!}{m_1! m_2! (n_1-m_1-q_{12})! (n_2-m_2-q_{12})! q_{12}!} \\ =& \prod_{i=1}^{2} \frac{n_i!}{m_i! (n_i - m_i - \sum_j q_{ij})! \prod_{j>i} q_{ij}!}. \end{aligned} \tag{S1}$$

If we consider particle 3 is also bonded into the cluster of particle 1 and 2 like in Fig. S1b, the number of possible combinations, W_3, is:

$$\begin{aligned} W_3 =& \binom{n_1}{m_1}\binom{n_1-m_1}{q_{12}}\binom{n_1-m_1-q_{12}}{q_{13}}\binom{n_2}{m_2}\binom{n_2-m_2}{q_{12}}\binom{n_2-m_2-q_{12}}{q_{23}} \\ & \binom{n_3}{m_3}\binom{n_3-m_3}{q_{13}}\binom{n_3-m_3-q_{13}}{q_{23}} q_{12}! q_{13}! q_{23}! \\ =& \frac{n_1! n_2! n_3!}{m_1! m_2! m_3! (n_1-m_1-q_{12}-q_{13})! (n_2-m_2-q_{12}-q_{23})! (n_3-m_3-q_{13}-q_{23})! q_{12}! q_{13}! q_{23}!} \\ =& \prod_{i=1}^{3} \frac{n_i!}{m_i! (n_i - m_i - \sum_j q_{ij})! \prod_{j>i} q_{ij}!}. \end{aligned} \tag{S2}$$

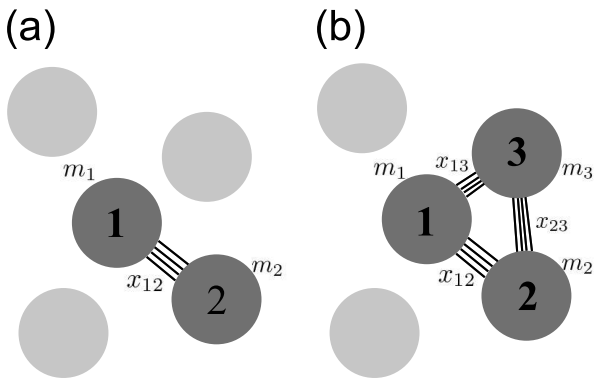

FIG. S1. Illustration of the number of possible bonds combinations in (a) 2-particles cluster and (b) 3-particle cluster.

We assume the total number of combinations of hybridization for a cluster of N particles is:

$$W_N = \prod_{i=1}^{N} \frac{n_i!}{m_i! (n_i - m_i - \sum_j q_{ij})! \prod_{j>i} q_{ij}!}. \tag{S3}$$

Then for the $(N+1)$-particle system, the number of combinations of hybridization W_{N+1} can be represented by the product of W_N and the combinations between the existing N particles with the $(N+1)$th particle:

$$W_{N+1} = W_N \binom{n_{N+1}}{m_{N+1}}$$

$$
\begin{aligned}
&\binom{n_{N+1}-m_{N+1}}{q_{1,N+1}}\binom{n_1-m_1-\sum_{j=1}^{N}q_{1,j}}{q_{1,N+1}}q_{1,N+1}!\\
&\binom{n_{N+1}-m_{N+1}-q_{1,N+1}}{q_{2,N+1}}\binom{n_2-m_2-\sum_{j=1}^{N}q_{2,j}}{q_{2,N+1}}q_{2,N+1}!\\
&\cdots\\
&\binom{n_{N+1}-m_{N+1}-\sum_{i=1}^{N-1}q_{i,N+1}}{q_{N,N+1}}\binom{n_N-m_N-\sum_{j=1}^{N}q_{N,j}}{q_{N,N+1}}q_{N,N+1}!\\
=&\left[\prod_{i=1}^{N}\frac{n_i!}{m_i!(n_i-m_i-\sum_j q_{ij})!\prod_{j>i}q_{ij}!}\right]\frac{n_{N+1}!}{m_{N+1}!(n_{N+1}-m_{N+1})!}\\
&\frac{(n_{N+1}-m_{N+1})!}{q_{1,N+1}!(n_{N+1}-m_{N+1}-q_{1,N+1})!}\frac{n_1-m_1-\sum_{j=1}^{N}q_{1,j}!}{q_{1,N+1}!(n_1-m_1-\sum_{j=1}^{N+1}q_{1,j})!}q_{1,N+1}!\\
&\frac{(n_{N+1}-m_{N+1}-q_{1,N+1})!}{q_{2,N+1}!(n_{N+1}-m_{N+1}-q_{1,N+1}-q_{2,N+1})!}\frac{n_2-m_2-\sum_{j=1}^{N}q_{2,j}!}{q_{2,N+1}!(n_2-m_2-\sum_{j=1}^{N+1}q_{2,j})!}q_{2,N+1}!\\
&\cdots\\
&\frac{(n_{N+1}-m_{N+1}-\sum_{i=1}^{N-1}q_{i,N+1})!}{q_{N,N+1}!(n_{N+1}-m_{N+1}-\sum_{i=1}^{N}q_{i,N+1})!}\frac{n_N-m_N-\sum_{j=1}^{N}q_{N,j}!}{q_{N,N+1}!(n_N-m_N-\sum_{j=1}^{N+1}q_{N,j})!}q_{N,N+1}!\\
=&\left(\prod_{i=1}^{N}\frac{n_i!}{m_i!\prod_{j>i}q_{ij}!}\right)\frac{n_{N+1}!}{(n_{N+1}-m_{N+1}-\sum_{i=1}^{N}q_{i,N+1})!}\left[\prod_{i=1}^{N}\frac{1}{q_{i,N+1}!(n_i-m_i-\sum_{j=1}^{N+1}q_{i,j})!}\right]\\
=&\prod_{i=1}^{N+1}\frac{n_i!}{m_i!(n_i-m_i-\sum_j q_{ij})!\prod_{j>i}q_{ij}!}.
\end{aligned}
\tag{S4}
$$

S2: PARTITION FUNCTIONS FOR LINKERS IN DIFFERENT STATES

As shown in Fig. S2, each linker can stay in three different states, i.e., free state, state a and state b. The partition function for the linker in free state ξ_{free} in the system of volume V can be written as

$$
\xi_{free}=\xi_{tran}\xi_{rot}=V\left(\frac{2\pi m_b}{\beta h^2}\right)^{3/2}\frac{8\pi^2 I}{\beta h^2}=\frac{1}{\Lambda^5}\frac{I}{m}4\pi V, \tag{S5}
$$

where Λ is de Broglie wavelength with I the moment of inertia for the stiff linker and h the Planck constant, and $\xi_{tran/rot}$ is the partition function for the translation/rotational entropy. $\beta=1/k_BT$ with k_B the Boltzmann constant and T the temperature of the system, respectively. Assuming $\frac{1}{\Lambda^5}\frac{I}{m}4\pi=1$ and considering the ideal gas of hard rods as the reference state, the canonical partition function $\mathcal{Z}$ and the free energy F of the ideal gas of N linkers can be written as

$$
\begin{aligned}
\mathcal{Z}&=\frac{\xi_{free}^N}{N!},\\
\beta F&=-\log\mathcal{Z}=-N\log\xi_{free}+N\log N-N,
\end{aligned}
\tag{S6}
$$

and the chemical potential of the linker is

$$
\mu=\frac{\partial F}{\partial N}=k_BT\log\rho, \tag{S7}
$$

with $\rho=N/V$ the density of the linkers. Because of the existence of colloidal particles, the free volume that linkers can explore decreases because of the excluded volume interaction between the linkers and the colloids. When two particles are close to each other, their depletion zones may overlap, which increases the free volume for the free linkers in the system and induces the depletion interaction between colloidal particles. When $R\gg l$, using Derjaguin

approximation [32], the depletion potential between two particles separated by the surface-surface distance h can be written with the first order approximation using the free linker concentration ρ_0 as [27]:

$$\beta U_{dep}(h) = \begin{cases} -\rho_0 \pi R \dfrac{(l-h)^3}{6l}, & 0 \le h \le l, \\ 0, & h > l. \end{cases} \tag{S8}$$

Besides the free linkers in the system, there are linkers bonded on the surface of colloidal particles, and the bonded linkers can stay in two different states, i.e., the state a and b in Fig. S2. The linkers in a state are essentially these linkers bonded on an mDNACC of complementary sequences with a free unbound end. The linkers in state b form bridges between two mDNACCs, and the two ends of the linkers are bonded to two different mDNACCs.

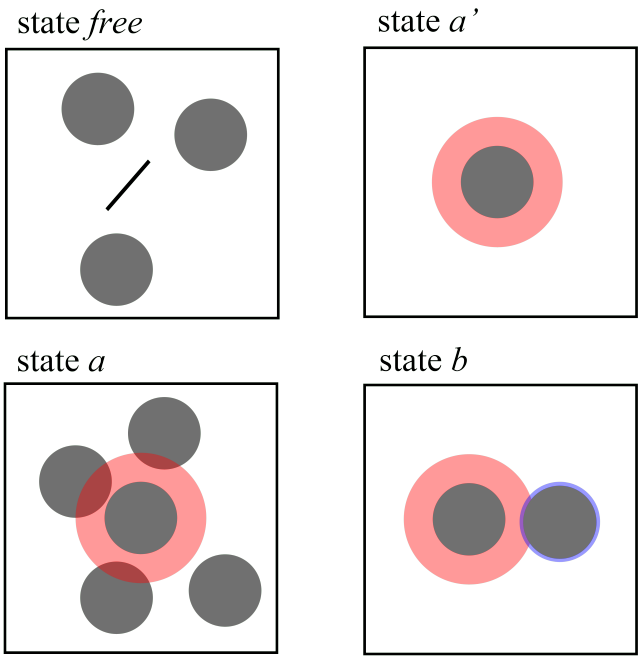

FIG. S2. Schematic representation for possible states of linkers. Top left: linkers are unbound and free in the system. Top right: linkers are bonded on a particle with a free end and not interacting with other particles. The red area is the volume that the free end can explore. Bottom left: linkers are bonded on a particle with a free end and interacting with other particles. Bottom right: linkers are bonded on two different particles and form a bridge. The blue area is the adsorption layer and purple area (overlap with red area) is the volume that other end explore when forming bridges.

In the dilute limit of mDNACCs, the linkers in state a do not interact with other particles, and we refer this special limit as state a'. Assume the particle that linker is bonded with is particle A, the partition function $\xi_{a'}$ for a single bonded linker can be written as:

$$\begin{aligned} \xi_{a'} &= \int e^{-\beta \Delta G_{bind}} \frac{d\omega}{h} \\ &= \int_R^{R+r_c} dr_A \int_{-\pi}^{\pi} 2\pi r_A^2 \sin\phi d\phi \delta(|\mathbf{r}_B - \mathbf{r}_A| - l) \Theta\left[|\chi \mathbf{r}_A + (1-\chi)\mathbf{r}_B| - R\right] \exp(-\beta \Delta G_{bind}), \qquad \forall \chi \in [0,1] \\ &= 2\pi \int_R^{R+r_c} r_A^2 (1+\cos\theta) dr_A \exp(-\beta \Delta G_{bind}) \end{aligned} \tag{S9}$$

where $\mathbf{r}_{A/B}$ is the position of A/B end of the linker. The Heaviside step function Θ ensures that the linker does not overlap with the particle, and the Dirac delta function ensures that the length of linker is fixed at l. Here $V_{a'} = 2\pi \int_R^{R+r_c} r_A^2 (1+\cos\theta) dr_A$ can be seen as the configurational volume that the linker in state a' can explore, and

θ is the minimum angle (see Fig. S3):

$$\cos\theta = \frac{r_A^2 + l'^2 - R^2}{2 r_A l'} \qquad \text{where} \qquad l' = \begin{cases} \sqrt{r_A^2 - R^2}, & r_A^2 - R^2 \geq l^2, \\ l, & r_A^2 - R^2 < l^2. \end{cases} \tag{S10}$$

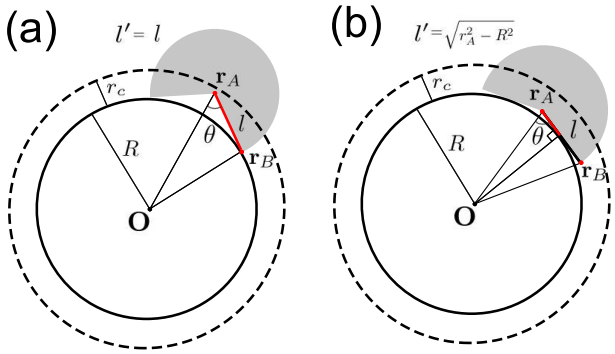

FIG. S3. Illustration for the calculation of Eq. S9. $\mathbf{r}_{A/B}$ is the position of A/B end of the linker with the length l, $\mathbf{r}_B$ here can move in grey district for given $\mathbf{r}_A$. l' is the minimun distance between $\mathbf{r}_A$ and the surface of the particle along the linker direction (red line). When $r_A^2 - R^2 < l^2$ (a), $\mathbf{r}_B$ can touch the surface of the particle without overlapping, and $l' = l$; otherwise (b) $\mathbf{r}_B$ can not reach the surface of the particle, and $l' = \sqrt{r_A^2 - R^2}$.

At a finite colloidal concentration, the existence of neighbouring colloids can influence the free volume of the bonded linkers with free ends, which induces a repulsive free energy βF_{rep}, and the partition function ξ_a for a single absorbed linker in state a is

$$\xi_a = \xi_{a'} \cdot e^{-\beta F_{rep}}. \tag{S11}$$

The probability $P(\mathbf{r}_B)$ for the free end of a linker at position $\mathbf{r}_B$ can be written as:

$$P(\mathbf{r}_B) = \int_R^{R+r_c} dr_A \int_{-\pi}^{\pi} d\phi \frac{2\pi r_A^2 \sin\phi}{4\pi r_A^2} \frac{\delta(|\mathbf{r}_B - \mathbf{r}_A| - l)}{2\pi(1+\cos\theta) l^2} \Theta\left[|\chi \mathbf{r}_A + (1-\chi)\mathbf{r}_B| - R\right] \qquad \forall \chi \in [0,1]. \tag{S12}$$

When $r_c/l \to 0$ and $l/R \to 0$, we can neglect the configuration space other than $\sqrt{R^2 + l^2} < r_B < R + l$ (consider the bonded end is grafted on the particle):

$$P(\mathbf{r}_B) = \begin{cases} \dfrac{1}{4\pi R^2 l}, & R^2 + l^2 < r^2 < (R+l)^2 \\ 0, & otherwise \end{cases} \tag{S13}$$

Here we assume $P(\mathbf{r}_B)$ to be *uniform*, and when $l/R \to 0$, the number of available states for the absorbed linkers is approximately proportional to the volume that the free end of linkers can explore [22]

$$\beta F_{rep} = -\log\left(\frac{\Omega_a}{\Omega_{tot}}\right) \approx -\log\left(\frac{V_{tot} - \sum V_{overlap}}{V_{tot}}\right), \tag{S14}$$

$$\xi_a = \xi_{a'} \cdot \frac{V_{tot} - \sum V_{overlap}}{V_{tot}}, \tag{S15}$$

where $V_{overlap}$ is the overlap volume between two spheres of radius $R_1 = R + l$ and of $R_2 = R$ with the center-to-center distance d, and V_{tot} is the volume that the free end of a bonded linker on an isolated colloid can explore:

$$V_{tot} = \frac{4}{3}\pi\left[(R+l)^3 - R^3\right] \approx 4\pi R^2 l, \tag{S16}$$

$$V_{overlap}(R_1, R_2, d) = \frac{\pi}{12d}(R_1 + R_2 - d)^2 \left[d^2 + 2d(R_1 + R_2) - 3(R_1^2 + R_2^2) + 6R_1R_2\right]. \tag{S17}$$

For the bridging linkers, the conformational free energy can be calculated by confining the free end of bonded linkers on the surface of the bridged particle. When the free end of a bonded linker bind with another colloid forming a bridge, the free end can only explore the overlapped volume between the adsorption layer of the bridged particle and the space that the free end may explore (the red area Fig.S2). Similar to βF_{rep}, the conformational free energy for bridging state βF_{cnf} can be written as

$$\beta F_{cnf} = -\log\left(\frac{\Omega_b}{\Omega_{tot}}\right) \approx -\log\left[\frac{V_b(R_1, R_2, r_c, d)}{2V_{tot}}\right], \tag{S18}$$

where $V_b(R_1, R_2, r_c, d)$ is the overlap volume between a sphere with radius R_1 and the adsorption layer of thickness r_c on the surface of another sphere with radius R_2 and the centre-to-centre distance between the two spheres is d:

$$\begin{aligned} V_b(R_1, R_2, r_c, d) = &[V_{overlap}(R_1 + l, R_2 + r_c, d) - V_{overlap}(R_1 + l, R_2, d)] \\ &- \left[V_{overlap}\left(\sqrt{R_1^2 + l^2}, R_2 + r_c, d\right) - V_{overlap}\left(\sqrt{R_1^2 + l^2}, R_2, d\right)\right]. \end{aligned} \tag{S19}$$

Then the partition function of a single linker bridging between two colloids is:

$$\xi_b = \xi_{a'} \cdot \exp\left[-(\beta\Delta G_{bind} + \beta F_{cnf})\right] = \xi_{a'} \cdot \exp\left(-\beta\Delta G_{bind}\right) \cdot \frac{V_b(R_1, R_2, r_c, d)}{2V_{tot}} \tag{S20}$$

S3: DERIVATION OF SELF-CONSISTENT EQUATION AND PROOF OF POSITIVE DEFINITENESS

Here we consider the probability of states having free unbound ssDNAs on the surface of particle i. $\bar{p}_i$ is the probability that a ssDNA is unbound:

$$\bar{p}_i + \frac{m_i}{n_i} + \sum_j \frac{q_{ij}}{n_i} = 1. \tag{S21}$$

Combining Eq.3 and Eq.S21, we can have a set of self-consistent equations:

$$\frac{1}{\bar{p}_i} = 1 + \xi_a e^{\beta\mu} + \sum_j \bar{p}_j n_j \xi_b e^{\beta\mu}. \tag{S22}$$

We employ the method in Ref [24] to prove that Eq. S22 has only one solution satisfying $0 < \bar{p}_i \leq 1$ for each i. We define $f(\bar{p}_i)$ as:

$$f(\bar{p}_i) = \sum_i (s_i\bar{p}_i - \log\bar{p}_i) + \frac{1}{2}\sum_{ij} \bar{p}_i k_{ij} \bar{p}_j, \tag{S23}$$

where $s_i = 1 + \xi_a e^{\beta\mu}$ and $k_{ij} = n_j \xi_b e^{\beta\mu}$. The stationary points of f are the solutions of Eq. S22:

$$\frac{\partial f}{\partial \bar{p}_i} = s_i - \frac{1}{\bar{p}_i} + \sum_{ij} k_{ij}\bar{p}_j = 0, \tag{S24}$$

which means the solutions are local optima of f. In the following, we prove that the Hessian matrix $H = \partial^2 f/\partial\bar{p}_i\partial\bar{p}_j$ is positively definite to prove the uniqueness of the solution of Eq. S22, by showing that $\sum_{ij} v_i(\partial^2 f/\partial\bar{p}_i\partial\bar{p}_j)v_j$ is positive for all non-zero vectors v_i:

$$\begin{aligned} \sum_{ij} v_i \left(\frac{\partial^2 f}{\partial\bar{p}_i\partial\bar{p}_j}\right) v_j &= \sum_{ij} v_i \left(\frac{1}{\bar{p}_i^2}\delta_{ij} + k_{ij}\right) v_j \\ &= \sum_{ij} \frac{v_i}{\bar{p}_i}(\delta_{ij} + \bar{p}_i k_{ij} \bar{p}_j)\frac{v_j}{\bar{p}_j}. \end{aligned} \tag{S25}$$

The ith diagonal element is:

$$|H_{ii}| = 1, \tag{S26}$$

and the sum of the off-diagonal terms in the ith row is

$$\sum_{j\neq i} |H_{ij}| = \sum_{j} \bar{p}_i k_{ij} \bar{p}_j = 1 - s_i \bar{p}_i < 1. \tag{S27}$$

Then for the ith row in Hessian matrix H:

$$|H_{ii}| - \sum_{j\neq i} |H_{ij}| > 0, \tag{S28}$$

which implies that the Hessian matrix h is *strictly diagonally dominant*, and it is positively definite.

S4: MEAN FIELD THEORY FOR LINKER-MEDIATED MDNACCS AT THE STRONG BINDING LIMIT $\beta\Delta G_{bind} \to -\infty$

For $\beta\Delta G_{bind} \to -\infty$, Eq.S22 leads to a diverging βF. We propose a new analytical form of effective interaction to simulate mDNACCs at the limit, by focusing on the effect of entropy. Essentially, when $\beta\Delta G_{bind} \to -\infty$, there is no available unbound site on colloids $\bar{n}_i = 0$, and

$$m_i = n_i - \sum_j q_{ij}. \tag{S29}$$

Combining Eq. 1 and Eq.S29, The partition function counting for all possible combinations of hybridization for $\{q_{ij}\}$ in the limit $\beta\Delta G_{bind} \to -\infty$, $Z_{\text{inf}}(\{q_{ij}\})$ can be written as:

$$Z_{\text{inf}}(\{q_{ij}\}) = \sum_{\{q_{ij}\}} W_{\text{inf}}(\{q_{ij}\}) \xi_a^{\sum_i m_i} \xi_b^{\sum_i \sum_{j>i} q_{ij}} e^{\beta\mu(\sum_i m_i + \sum_i \sum_{j>i} q_{ij})}, \tag{S30}$$

where $W_{\text{inf}}(\{q_{ij}\})$ is the combinational term with Eq.S29:

$$W_{\text{inf}}(\{q_{ij}\}) = \prod_i \frac{n_i!}{(n_i - \sum_j q_{ij})! \sum_{j>i} q_{ij}!}. \tag{S31}$$

Here we extract the $\exp(-\beta\Delta G_{bind})$ term from $\xi_{a/b}$, to focus on the effect of entropy:

$$\xi_a^* = \xi_a e^{\beta\Delta G_{bind}}, \tag{S32}$$

and

$$\xi_b^* = \xi_b e^{2\beta\Delta G_{bind}}. \tag{S33}$$

With Stirling approximation and substituting Eq.S29 and Eq.S38, we can write the partition function $Z_{\text{inf}}(\{q_{ij}\})$ as:

$$Z_{\text{inf}} = \sum_{\{q_{ij}\}} \exp\left(-\beta\mathcal{F}_{\text{inf}}(\{q_{ij}\})\right), \tag{S34}$$

$$\beta\mathcal{F}_{\text{inf}} = \sum_i \left[m_i \log \frac{m_i}{\xi_a^* e^{\beta\mu}} + \sum_{j>i} q_{ij} \left(\log \frac{q_{ij}}{\xi_b^* e^{\beta\mu}} + 1 \right) + n_i \left(\beta\Delta G_{bind} - \log n_i \right) \right], \tag{S35}$$

using the saddle point approximation, we obtain

$$\frac{\partial \mathcal{F}_{\text{inf}}(\{q_{ij}\})}{\partial \{q_{ij}\}} = 0, \tag{S36}$$

by introducing $q_{ij} = q_{ji}$ into Eq.S36, we have

$$q_{ij} = m_i m_j \Xi_{ab}, \tag{S37}$$

when Ξ_{ab} is the entropy penalty of a bridging linker (state b) transforms to two bonded linkers with free ends (state a):

$$\Xi_{ab} = \frac{\xi_b^*}{\xi_a^{*2}} e^{-\beta\mu}. \tag{S38}$$

For each particle i,

$$p_i^a + \sum_j \frac{q_{ij}}{n_i} = 1, \tag{S39}$$

with $p_i^a = m_i/n_i$, and we can have a set of self-consistent equations:

$$p_i^a = \frac{1}{1 + \sum_j n_j p_j \Xi_{ab}}. \tag{S40}$$

Combining Eq.S35 and Eq.S37, the free energy of mDNACCs system in the limit of $\beta\Delta G_{bind} \to -\infty$, βF_{inf}, can be written by:

$$\beta F_{\text{inf}} = \sum_i \left[n_i \log \frac{p_i^a}{\xi_a^* e^{\beta\mu}} + \frac{1}{2} \sum_j q_{ij} + n_i \left(\beta\Delta G_{bind}\right) \right] + \beta U_{dep}. \tag{S41}$$

According to the method in Ref [24] the Hessian matrix $\left[\frac{\partial^2 \beta F_{\text{inf}}}{\partial q_{ij} \partial q_{i'j'}}\right]$ is always positively definite, and βF_{inf} is a convex function, which implies that there is only one solution satisfying $0 < p_i^a \leq 1$ for each i in Eq.S40.