ELECTRONIC SUPPLEMENTARY INFORMATION

Theory and Simulations of Light-Induced Self-Assembly in Colloids with Quantum Chemistry Derived Empirical Potentials

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SUPPORTING METHODS

Discrete and Analytical Derivations for $\mathcal{U}(r_{12}) = 1$

Discrete Method

The effective interaction between two ligand-coated NPs is given by the summation of the interaction energy between all ligand-ligand pairs on the interacting hemispheres in vicinity (see Figure 4A and Equation 1). We substitute $\mathcal{U}(r_{12}) = 1$ to obtain:

$$U(d) = \sum_{i=1}^{N_{lig}} \sum_{j=1}^{N_{lig}} \mathcal{U}(r_{12}) = \sum_{i=1}^{N_{lig}} \sum_{j=1}^{N_{lig}} 1 = \frac{N_{lig}^2}{4} = \frac{20 \times 20}{4} \quad \text{(for $N_{lig} = 20$)} = 100 \quad \text{(S1)}$$

Analytical Method

The effective interaction between two ligand-coated NPs is given by integrating over the interacting hemispheres in vicinity (see Figure 4C and and Equation 4). Substituting $\mathcal{U}(r_{12}) = 1$ in Equation 4, we get:

$$U(d) = \rho^2 \int_{S_1} \int_{S_2} \mathcal{U}(r_{12}) dS_1 dS_2$$

$$= \rho^2 \int_{S_1} dS_1 \int_{S_2} dS_2 \mathcal{U}(r_{12})$$

$$= \rho^2 \left[ R^2 \int_0^{2\pi} d\theta_1 \int_0^{\pi/2} sin\phi_1 d\phi_1 \right] \left[ R^2 \int_0^{2\pi} d\theta_2 \int_0^{\pi/2} sin\phi_2 d\phi_2 \right] \mathcal{U}(r_{12})$$

$$= \frac{N_{lig}^2}{(4\pi R^2)^2} \left[ R^2 \int_0^{2\pi} d\theta_1 \int_0^{\pi/2} sin\phi_1 d\phi_1 \right] \left[ R^2 \int_0^{2\pi} d\theta_2 \int_0^{\pi/2} sin\phi_2 d\phi_2 \right] \left[ \mathcal{U}(r_{12}) \right]$$

$$= \frac{N_{lig}^2}{(4\pi R^2)^2} \left[ R^2 \left[ \theta_1 \right]_0^{2\pi} \left[ -cos\phi_1 \right]_0^{\pi/2} \right] \left[ R^2 \left[ \theta_2 \right]_0^{2\pi} \left[ -cos\phi_2 \right]_0^{\pi/2} \right] \left[ \mathcal{U}(r_{12}) \right]$$

$$= \frac{N_{lig}^2}{16\pi^2 R^4} \left[ R^2 \times 2\pi \times 1 \right] \left[ R^2 \times 2\pi \times 1 \right] \left[ \mathcal{U}(r_{12}) \right]$$

$$= \frac{N_{lig}^2}{4}$$

$$= \frac{20 \times 20}{4} \quad \text{(for $N_{lig} = 20$)}$$

$$= 100 \quad \text{(S2)}$$
Figure S1: Schematic representations of the possible conformations for trans-NPs. (A) At $d = 0$, the extended thiol chain shell (orange) overlaps with the DDA/DDAB shell (gray) of the other particle and hence this conformation is energetically not favorable. (B) At $d \geq L_{\text{lig}}/2$, the conformation is energetically feasible.
Figure S2: A schematic representation of (A) a trans-NP showing a flexible ADT ligand in comparison to fully extended ligands. (B) The traces of the effective interaction energy for a pair of trans-NPs at different values of the functional ligand length $L_{\text{lig}}$. At $L_{\text{lig}} = 20$, the interaction energy shows a negative value for certain values of $d$, and could be considered valid. At $L_{\text{lig}} = 25$, the interaction energy still shows a negative value for certain values of $d$, but its magnitude can be considered to be negligible.
Figure S3: Morphologies for *cis*-NP (pink) and *trans*-NP (blue) systems at various values of $T^*$ and $\rho^*$. The snapshots enclosed in the orange box are shown in Figure 6.
Figure S4: Radial distribution functions. (A) $\rho^* = 1.25 \times 10^{-4}$, (B) $\rho^* = 1.00 \times 10^{-3}$, and (C) $\rho^* = 8.00 \times 10^{-3}$. 
Figure S5: Average cluster size with respect to time steps. (A) $\rho^* = 1.25 \times 10^{-4}$ and (B) $\rho^* = 2.96 \times 10^{-4}$.

Figure S6: Distributions of the cluster size. (A) $\rho^* = 1.25 \times 10^{-4}$ and (B) $\rho^* = 2.96 \times 10^{-4}$. 
Figure S7: Morphologies for cis-NP systems at various values of reduced density ($\rho^*$) obtained from simulated annealing simulations.