Supporting Information

Quantitative Modeling of Self-Assembly Growth of Luminescent Colloidal $CH_3NH_3PbBr_3$ Nanocrystals

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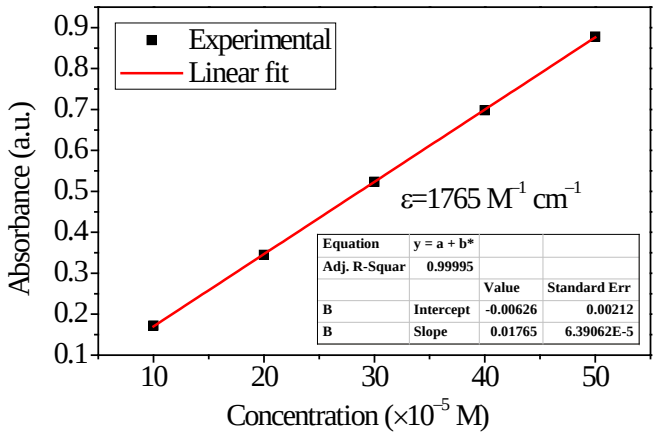

Figure S1. Plot of absorbance of different $MAPbBr_3$ QD solutions at $\lambda = 448$ nm as a function of concentration.

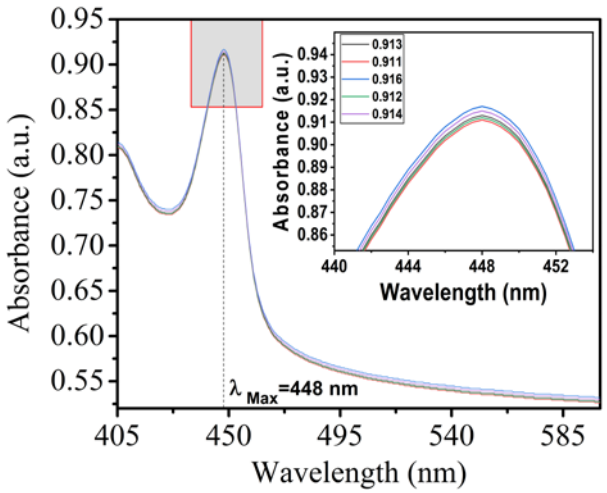

Figure S2. UV–vis absorption spectra of five batches of $MAPbBr_3$ QD solutions prepared using the same method. Inset shows enlarged region.

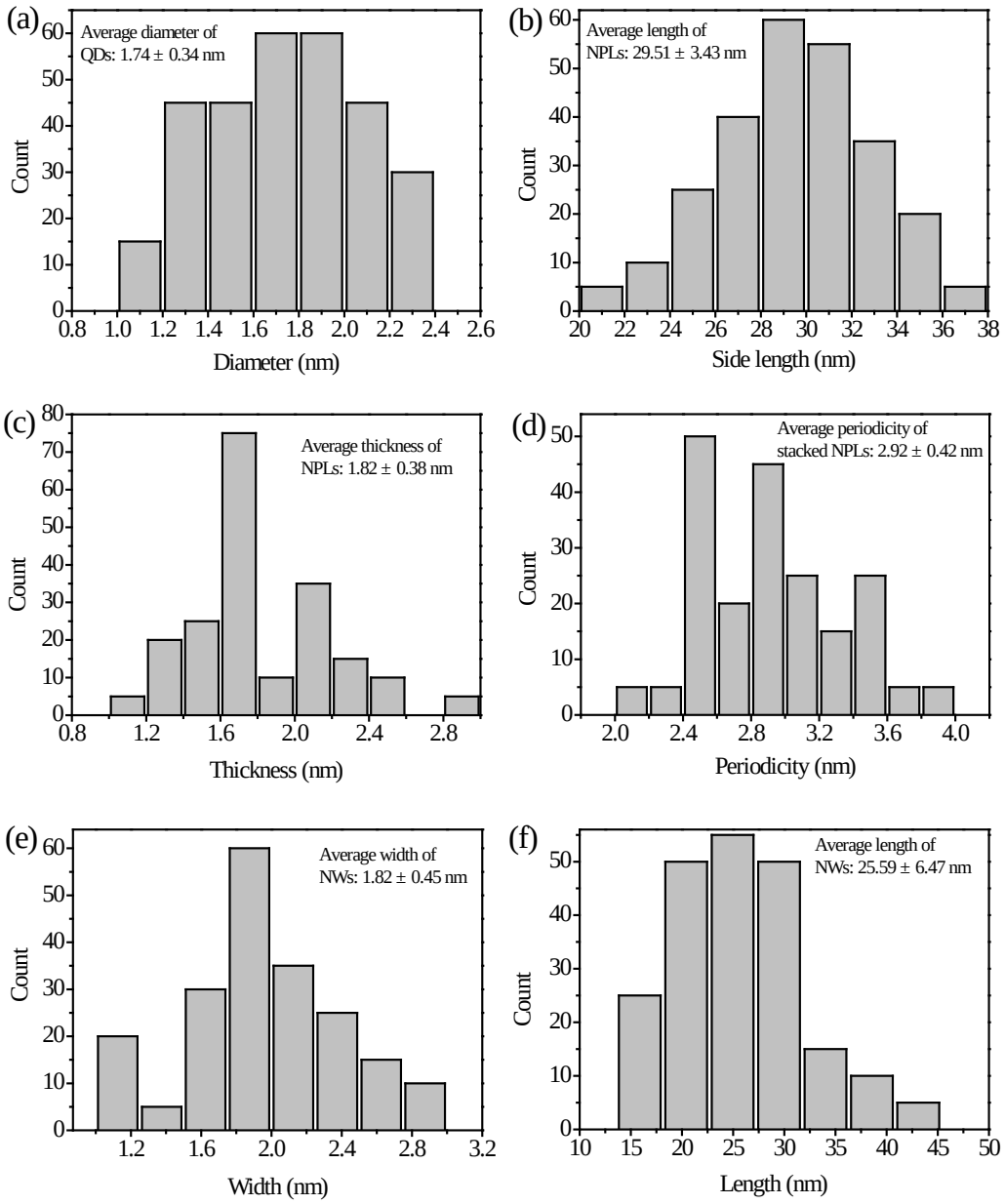

Figure S3. Size distribution histograms of $MAPbBr_3$ QDs, NWs, and NPLs.

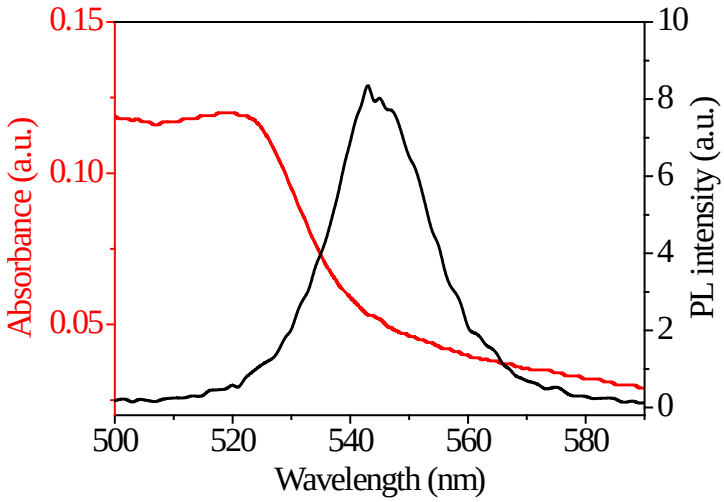

Figure S4. UV–vis absorption spectrum and PL spectrum (excitation: 360 nm) of $MAPbBr_3$ bulk crystal.

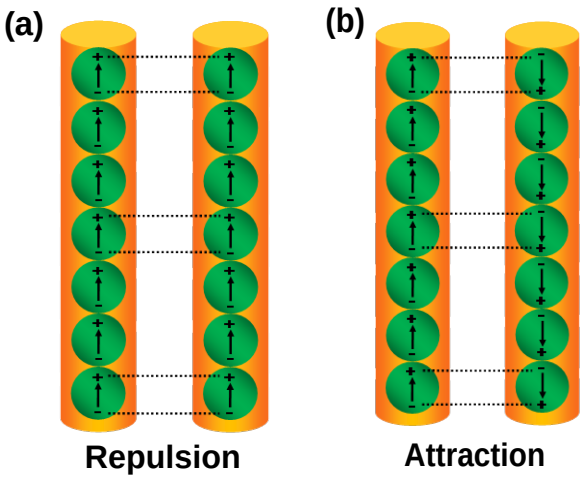

Figure S5. Schematic diagram of repulsive/attractive force between NWs in the case of parallel and anti-parallel electric dipoles.

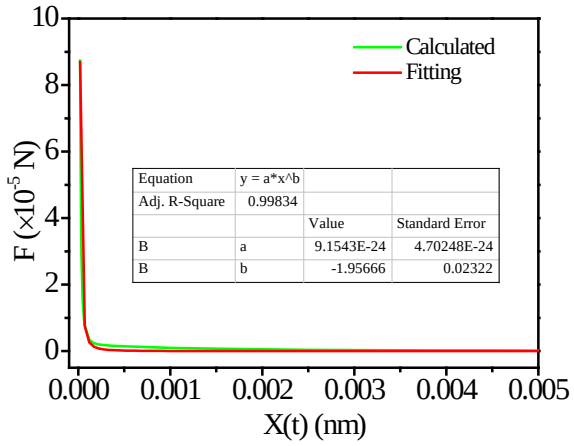

Figure S6. Calculated and fitted polarization force as function of separation for two attracting NPLs in liquid medium.

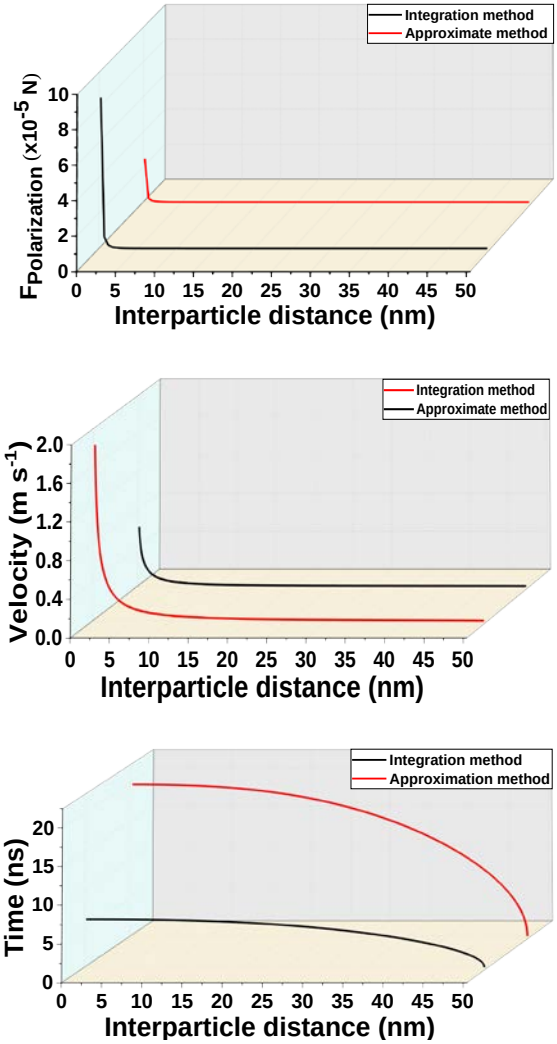

Figure S7. Curves of F–x, v–x, and t–x for two approaching $MAPbBr_3$ NPLs obtained by using integration method and approximation method, respectively.

Details of the calculations

(1) Calculation of effective permittivity

To calculate the effective permittivity, we should take into account the perovskite core, the organic capping ligands, and the surrounding solvent. According to the previous study,[1,2] the effective permittivity between two interacting particles can be estimated using the following formula:

$$\log\varepsilon_{\text{eff}} = v_1\log\varepsilon_1 + v_2\log\varepsilon_2 + v_3\log\varepsilon_3, \quad (1)$$

where $\varepsilon_1 = 1000$ is the dielectric constant of $CH_3NH_3PbBr_3$, ε_2 and ε_3 represent the dielectric constants of the capping ligands (3.63 for n-octylamine) and the surrounding solvent (2.38 for n-hexane), respectively. v_1, v_2, and v_3 are the corresponding volume fractions:

$$v_1 = \frac{4d^3}{(d+h_0)^2(3Y+2d+4h_0)}, \quad (2)$$

$$v_2 = \frac{4[(d+2h_0)^3-d^3]}{(d+2h_0)^2(3Y+2d+4h_0)}, \quad (3)$$

$$v_3 = \frac{3Y-2d-4h_0}{3Y+2d+4h_0}, \quad (4)$$

where d is the diameter of the $CH_3NH_3PbBr_3$ nanoparticle, d = 1.74 ± 0.34 nm, h_0 is the length of the capping ligand, and Y is the center-to-center separation of the two interacting nanoparticles.

(2) Calculation of Debye length

$$\kappa = \left(\frac{4\pi e^2 Z^2 n_{\text{i}}}{\varepsilon_0\varepsilon_{\text{eff}}k_{\text{B}}T}\right)^{1/2}, \quad (5)$$

where e is the electron charge, Z is the valence of the $MAPbBr_3$ QD, and n_{i} is its equilibrium concentration in the solution. ε_0 is the permittivity in vacuum, ε_{eff} is the effective permittivity, k_{B} is the Boltzmann constant, and the temperature $T = 300$ K.

(3) Calculation of effective Hamaker constant

The effective Hamaker constant A_{131}, A_{232}, and A_{123} can be calculated by using the following formulae:[3]

$$A_{232} = \frac{3k_{\text{B}}T}{4}\left[\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right]^2 + \frac{3h\nu_{\text{e}}}{16\sqrt{2}}\frac{\left(n_2^2-n_3^2\right)^2}{\left(n_2^2+n_3^2\right)^{3/2}}, \quad (6)$$

$$A_{131} = \frac{3k_{\text{B}}T}{4}\left[\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right]^2 + \frac{3h\nu_{\text{e}}}{16\sqrt{2}}\frac{\left(n_1^2-n_3^2\right)^2}{\left(n_1^2+n_3^2\right)^{3/2}}, \quad (7)$$

$$A_{123} = \frac{3k_{\text{B}}T}{4}\left[\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right]\left[\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right] + \frac{3h\nu_e}{8\sqrt{2}}\frac{(n_1{}^2-n_3{}^2)(n_2{}^2-n_3{}^2)}{\sqrt{(n_1{}^2+n_3{}^2)(n_2{}^2+n_3{}^2)}[\sqrt{n_1{}^2+n_3{}^2}+\sqrt{n_2{}^2+n_3{}^2}]}, \quad (8)$$

where ε_{i} is the static relative permittivity, h is the Planck's constant, ν_{e} is the main electronic absorption frequency in the UV region. n_{i} is the refractive index in the visible region. For the $MAPbBr_3$ QDs and NWs, $\varepsilon_1 = 1000$,[4] $\varepsilon_2 = 3.63$ and $\varepsilon_3 = \varepsilon_{\text{toluene}} = 2.38$, $\nu_{\text{e}} = 7.09 \times 10^{14}$ Hz, $n_1 = 2.55$,[5] $n_2 = n_{\text{Octylamine}} = 1.43$

and $n_3 = n_{\text{toluene}} = 1.50$. For the $MAPbBr_3$ NPLs, the main electronic absorption frequency in the UV region $\nu_e = 6.34\times10^{14}$ Hz, as obtained from the UV–vis absorption spectrum.

(4) Calculation based on DLVO theory

For $MAPbBr_3$ QDs: The pure stoichiometric $MAPbBr_3$ QD without surface ligands should have negligible surface charges. However, some study has suggested that the $MAPbBr_3$ QD might possess a Br^--rich surface.[6] The surface charge of such $MAPbBr_3$ QD with Br^--rich surface can be estimated (note that the surface charges will change if there are organic ligands). Hence we estimate the charge of $MAPbBr_3$ QD by using the method of Ref. 6. The surface charge will be changed when there are enough surface organic ligands.

For $MAPbBr_3$ NWs: The attraction energy between two adjacent $MAPbBr_3$ NWs is the van der Waals force-related energy:

$$W_{\text{A}} = \text{W}_{\text{vdW}} = -\frac{A_{\text{eff}}LR^2}{48\sqrt{2}x(t)^{3/2}}. \quad (9)$$

The repulsion energy consists of the electrostatic interaction energy[7] and the steric energy of surface ligands:[8]

$$W_{\text{R}} = W_{\text{E}} + W_{\text{RS}} = \frac{R}{2} \times Z \times e^{-\kappa x(t)} + \Delta f \cdot S, \quad (10)$$

where $Z = 64\pi\varepsilon_0\varepsilon_{\text{eff}}\left(\frac{k_{\text{B}}T}{e}\right)^2 \tanh^2\left(\frac{e\psi_0}{4k_{\text{B}}T}\right)$, $\psi_0 = \frac{\sigma}{\varepsilon_0\varepsilon_{\text{eff}}\kappa}$, σ is the surface charge density of $MAPbBr_3$. S is the shadow area of the nanowire on the screen normal to its velocity. $\Delta f = 2[f\left(\frac{x(t)}{2}\right) - f(h_0)]$ （$0 < \text{x(t)} \le 2h_0$）is the steric energy per unit area. And the free energy of the ligand layer per unit area is

$$f(\text{x(t)}) = \frac{\pi^2 k_{\text{B}}T\Gamma {h_0}^2}{6NB^2}\left[\frac{1}{2}\left(\frac{h_0}{\text{x(t)}}\right) + \frac{1}{2}\left(\frac{\text{x(t)}}{h_0}\right)^2 - \frac{1}{10}\left(\frac{\text{x(t)}}{h_0}\right)^5\right], \quad (11)$$

where Γ is the grafting density of the organic ligands, N is the number of the Kuhn monomers, and B is the characteristic length of the ligand chain.

For $MAPbBr_3$ NPLs: The attractive energy consists of the polarization force-related energy and the van der Waals force-related energy. The polarization force energy can be deduced using the formula of the polarization force between two NPLs, which is obtained by using the integration method. The van der Waals force energy of two attracting NPLs is

$$\text{W}_{\text{vdW}} = -\frac{S}{12\pi}\left[\frac{A_{232}}{x(t)^2} - \frac{2A_{123}}{(x(t)+h_0)^2} + \frac{A_{131}}{(x(t)+2h_0)^2}\right]. \quad (12)$$

The repulsion energy consists of the electrostatic interaction energy and the steric energy of surface ligands. The formula of the electrostatic interaction energy of two adjacent NPLs is $W_{\text{E}} = (\kappa/2\pi)Ze^{-\kappa x(t)}$, and the steric energy of the ligands on the NPL surface can be calculated using the same method as that used in the case of the NWs.

Note: The movement duration time and velocity of two attracting $MAPbBr_3$ NCs driven by the polarization force or by the van der Waals force (Figure 5) as well as the

interaction energy between them (Figure 6) are calculated using MATLAB R2015b.

References

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