Ligand-mediated nanocluster formation with classical and autocatalytic growth

Mohsen Farshad,[‡] Dylan Suvlu,[‡] and Jayendran C. Rasaiah[*]

Department of Chemistry, University of Maine, Orono, Maine 04469, United States

Supporting Information

List of Symbols

$k_{p,1}$	Monomer formation rate coefficient, s^{-1}
$k_{p,2}$	Reduction of ligand-associated monomer ion rate coefficient, s^{-1}
$k_{b,1}$	Ligand binding to metal atom rate coefficient, M^{-1} s^{-1}
$k_{ub,1}$	Ligand unbinding to metal atom rate coefficient, s^{-1}
$k_{b,2}$	Ligand binding to metal ion rate coefficient, M^{-1} s^{-1}
$k_{ub,2}$	Ligand unbinding to metal ion rate coefficient, s^{-1}
k_n	Self-dimerization rate coefficient, M^{-1} s^{-1}
$k_{n,ac}$	Autocatalytic dimerization rate coefficient, M^{-1} s^{-1}
k_g	Monomer addition growth rate coefficient, M^{-1} s^{-1}
k_d	Monomer dissociation rate coefficient, s^{-1}
$k_{g,ac}$	Autocatalytic growth rate coefficient, M^{-1} s^{-1}
$k_{d,ac}$	Autocatalytic dissociation rate coefficient, s^{-1}
k_a	Ligand association rate coefficient, M^{-1} s^{-1}
k_e	Ligand elimination rate coefficient, s^{-1}
t	Time of reaction, s
i	Number of monomers, $-$

j	Number of ligands, $-$
$[\mathrm{M}^+]$	Concentration of metal ion, M
$[\mathrm{M}]$	Concentration of metal atom, M
$[\mathrm{L}]$	Concentration of Ligand, M
$[\mathrm{ML}]$	Concentration of ligand associated metal atom, M
$[\mathrm{ML}^+]$	Concentration of ligand associated metal ion, M
$[\mathrm{C}_{2,j}]$	Concentration of dimer with *j* ligands, M
$[\mathrm{C}_{i,j}]$	Concentration of cluster with *i* monomers and *j* ligands, M
$[\bar{\mathrm{C}}_i]$	Concentration of cluster with *i* monomers regardless of number of *j* ligands, M
$[\bar{\mathrm{L}}_i]$	First order moment, M
$[\bar{\bar{\mathrm{L}}}_i]$	Second order moment, M
$N_{s,i}$	Number of sites on a cluster with i monomers, $-$
$p(j\,|\,i)$	probability of finding *j* ligands on a given cluster of *i* monomers, $-$
p_i	probability of finding a bound ligand with on a cluster with *i* monomers, $-$
$\mathrm{C}(i,t)$	Monomeric concentration of clusters with *i* monomers at time *t*, M
$\mathrm{C}(D,t)$	Concentration of cluster with *i* monomers at time *t*, M
D_M	Monomer diameter, m

Here we present the rate equations in our model before and after applying method of moments.[1] The reaction scheme is reproduced below:

$$\mathrm{M}^+ \xrightarrow{k_{p,1}} \mathrm{M} \text{ ; Monomer formation} \quad \text{(S1a)}$$

$$\mathrm{M} + \mathrm{L} \underset{k_{ub,1}}{\overset{k_{b,1}}{\rightleftharpoons}} \mathrm{ML} \text{ ; Ligand association with metal atom} \quad \text{(S1b)}$$

$$\mathrm{M}^+ + \mathrm{L} \underset{k_{ub,2}}{\overset{k_{b,2}}{\rightleftharpoons}} \mathrm{ML}^+ \text{ ; Ligand association with metal ions} \quad \text{(S1c)}$$

$$\mathrm{ML}^+ \xrightarrow{k_{p,2}} \mathrm{ML} \text{ ; Monomer formation} \quad \text{(S1d)}$$

$$\mathrm{ML} + \mathrm{ML} \xrightarrow{k_n} \mathrm{C}_{2,2} \text{ ; Self-dimerization} \quad \text{(S1e)}$$

$$\mathrm{ML} + \mathrm{ML}^+ \xrightarrow{k_{n,ac}} \mathrm{C}_{2,2} \text{ ; Autocatalytic dimerization} \quad \text{(S1f)}$$

$$\mathrm{C}_{i,j} + \mathrm{ML} \underset{k_{d,j+1}}{\overset{k_{g,i,j}}{\rightleftharpoons}} \mathrm{C}_{i+1,j+1} \text{ ; Monomer addition growth} \quad \text{(S1g)}$$

$$\mathrm{C}_{i,j} + \mathrm{ML}^+ \underset{k_{d,j+1,ac}}{\overset{k_{g,i,j,ac}}{\rightleftharpoons}} \mathrm{C}_{i+1,j+1} \text{ ; Autocatalytic growth} \quad \text{(S1h)}$$

$$\mathrm{C}_{i,j} + \mathrm{L} \underset{k_{e,j+1}}{\overset{k_{a,i,j}}{\rightleftharpoons}} \mathrm{C}_{i,j+1} \text{ ; Ligand association/elimination to cluster} \quad \text{(S1i)}$$

The minimum value of i is 2 and the maximum was set to 400 in calculations. The rate equations before applying method of moments of the above model are as follows:

$$\frac{d[\mathrm{M}^+]}{dt} = -k_{p,1}[\mathrm{M}^+] - k_{b,1}[\mathrm{M}^+][\mathrm{L}] + k_{ub,1}[\mathrm{ML}^+] \quad \text{(S2)}$$

$$\frac{d[\mathrm{M}]}{dt} = k_{p,1}[\mathrm{M}^+] - k_{b,2}[\mathrm{M}][\mathrm{L}] + k_{ub,2}[\mathrm{ML}] \quad \text{(S3)}$$

$$\frac{d[\mathrm{L}]}{dt} = -k_{b,1}[\mathrm{M}][\mathrm{L}] + k_{ub,1}[\mathrm{ML}] - k_{b,2}[\mathrm{M}^+][\mathrm{L}] + k_{ub,2}[\mathrm{ML}^+] - k_a[\mathrm{L}]\sum_{i=2}^{i_{\max}}\sum_{j=0}^{N_{s,i}}[\mathrm{C}_{i,j}](N_{s,i} - j) + k_e\sum_{i=2}^{i_{\max}}\sum_{j=0}^{N_{s,i}}[\mathrm{C}_{i,j}]j \quad \text{(S4)}$$

$$\frac{d[\mathrm{ML}]}{dt} = k_{p,2}[\mathrm{ML}^+] + k_{b,1}[\mathrm{M}][\mathrm{L}] - k_{ub,1}[\mathrm{ML}] - 2k_n[\mathrm{ML}]^2 - k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - k_g[\mathrm{ML}]\sum_{i=2}^{i_{\max}}\sum_{j=0}^{N_{s,i}}[\mathrm{C}_{i,j}](N_{s,i} - j) + k_d\sum_{i=3}^{i_{\max}}\sum_{j=0}^{N_{s,i}}[\mathrm{C}_{i,j}]j \quad \text{(S5)}$$

$$\frac{d[\mathrm{ML}^+]}{dt} = k_{b,2}[\mathrm{M}^+][\mathrm{L}] - k_{ub,2}[\mathrm{ML}^+] - k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - k_{g,ac}[\mathrm{ML}^+]\sum_{i=2}^{i_{\max}}\sum_{j=0}^{N_{s,i}}[\mathrm{C}_{i,j}](N_{s,i} - j) + k_{d,ac}\sum_{i=3}^{i_{\max}}\sum_{j=0}^{N_{s,i}}[\mathrm{C}_{i,j}]j \tag{S6}$$

$$\frac{d}{dt}[\mathrm{C}_{2,2}] = k_n[ML]^2 + k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - (k_g[\mathrm{ML}] + k_{g,ac}[\mathrm{ML}^+])[\mathrm{C}_{2,2}](N_{s,2} - 2) + (k_d + k_{d,ac})3[\mathrm{C}_{3,3}] - k_a[L]\{[\mathrm{C}_{2,2}](N_{s,2} - 2) - [\mathrm{C}_{2,1}](N_{s,2} - 1)\} + k_e\{3[\mathrm{C}_{2,3}] - 2[\mathrm{C}_{2,2}]\} \tag{S7}$$

$$\frac{d}{dt}[\mathrm{C}_{i,j}] = -(k_g[\mathrm{ML}] + k_{g,ac}[\mathrm{ML}^+])\{[\mathrm{C}_{i,j}](N_{s,i} - j) - [\mathrm{C}_{i-1,j-1}](N_{s,i-1} - j + 1)\} + (k_d + k_{d,ac})\{[\mathrm{C}_{i+1,j+1}](j+1) - [\mathrm{C}_{i,j}]j\} - k_a[L]\{[\mathrm{C}_{i,j}](N_{s,i} - j) - [\mathrm{C}_{i,j-1}](N_{s,i} - j + 1)\} + k_e\{[\mathrm{C}_{i,j+1}](j+1) - [\mathrm{C}_{i,j}]j\} \qquad 3 \le i \le 400 \tag{S8}$$

As described in the main text, we used method of moments to convert the equations with two internal coordinates (2-D) to two one internal coordinates (1-D). The full set of equations used for calculations are as follows

$$\frac{d[\mathrm{M}^+]}{dt} = -k_{p,1}[\mathrm{M}^+] - k_{b,1}[\mathrm{M}^+][\mathrm{L}] + k_{ub,1}[\mathrm{ML}^+] \tag{S9}$$

$$\frac{d[\mathrm{M}]}{dt} = k_{p,1}[\mathrm{M}^+] - k_{b,2}[\mathrm{M}][\mathrm{L}] + k_{ub,2}[\mathrm{ML}] \tag{S10}$$

$$\frac{d[\mathrm{L}]}{dt} = -k_{b,1}[\mathrm{M}][\mathrm{L}] + k_{ub,1}[\mathrm{ML}] - k_{b,2}[\mathrm{M}^+][\mathrm{L}] + k_{ub,2}[\mathrm{ML}^+] - k_a[\mathrm{L}]\sum_{i=2}^{i_{\max}}\{[\bar{\mathrm{C}}_i]N_{s,i} - [\bar{\mathrm{L}}_i]\} + k_e\sum_{i=2}^{i_{\max}}[\bar{\mathrm{L}}_i] \tag{S11}$$

$$\frac{d[\mathrm{ML}]}{dt} = k_{p,2}[\mathrm{ML}^+] + k_{b,1}[\mathrm{M}][\mathrm{L}] - k_{ub,1}[\mathrm{ML}] - 2k_n[\mathrm{ML}]^2 - k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - k_g[\mathrm{ML}]\sum_{i=2}^{i_{\max}}\{[\bar{\mathrm{C}}_i]N_{s,i} - [\bar{\mathrm{L}}_i]\} + k_d\sum_{i=3}^{i_{\max}}[\bar{\mathrm{L}}_i] \tag{S12}$$

$$\frac{d[\mathrm{ML}^+]}{dt} = -k_{p,2}[\mathrm{ML}^+] + k_{b,2}[\mathrm{M}^+][\mathrm{L}] - k_{ub,2}[\mathrm{ML}^+] - k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - k_{g,ac}[\mathrm{ML}^+]\sum_{i=2}^{i_{\max}}\{[\bar{\mathrm{C}}_i]N_{s,i} - [\bar{\mathrm{L}}_i]\} + k_{d,ac}\sum_{i=3}^{i_{\max}}[\bar{\mathrm{L}}_i] \tag{S13}$$

$$\frac{d}{dt}[\overline{\mathrm{C}}_2] = k_n[\mathrm{ML}]^2 + k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - (k_g[\mathrm{ML}] + k_{g,ac}[\mathrm{ML}^+])\{[\overline{\mathrm{C}}_2]N_{s,2} - [\overline{\mathrm{L}}_2]\}$$
$$+(k_d + k_{d,ac})[\overline{\mathrm{L}}_3] \tag{S14}$$

$$\frac{d}{dt}[\overline{\mathrm{L}}_2] = k_n[\mathrm{ML}]^2 + k_{n,ac}[\mathrm{ML}][\mathrm{ML}^+] - (k_g[\mathrm{ML}] + k_{g,ac}[\mathrm{ML}^+])\{[\overline{\mathrm{L}}_2]N_{s,2} - [\overline{\overline{\mathrm{L}}}_2]\}$$
$$+(k_d + k_{d,ac})\{[\overline{\overline{\mathrm{L}}}_3] - [\overline{\mathrm{L}}_3]\} - k_a[\mathrm{L}]\{[\overline{\mathrm{C}}_2]N_{s,2} - [\overline{\mathrm{L}}_2]\} - k_e[\overline{\mathrm{L}}_2] \tag{S16}$$

$$\frac{d}{dt}[\overline{\mathrm{C}}_i] = -(k_g[\mathrm{ML}] + k_{g,ac}[\mathrm{ML}^+])\{([\overline{\mathrm{C}}_i]N_{s,i} - [\overline{\mathrm{L}}_i]) - ([\overline{\mathrm{C}}_{i-1}]N_{s,i-1} - [\overline{\mathrm{L}}_{i-1}])\}$$
$$+(k_d + k_{d,ac})\{[\overline{\mathrm{L}}_{i+1}] - [\overline{\mathrm{L}}_i]\} \qquad 3 \le i \le 400 \tag{S17}$$

$$\frac{d}{dt}[\overline{\mathrm{L}}_i] = -(k_g[\mathrm{ML}] + k_{g,ac}[\mathrm{ML}^+])\{([\overline{\mathrm{L}}_i]N_{s,i} - [\overline{\overline{\mathrm{L}}}_i]) - ([\overline{\mathrm{C}}_{i-1}]N_{s,i-1} + [\overline{\mathrm{L}}_{i-1}](N_{s,i-1} - 1) - [\overline{\overline{\mathrm{L}}}_{i-1}])\}$$
$$+(k_d + k_{d,ac})\{([\overline{\overline{\mathrm{L}}}_{i+1}] - [\overline{\mathrm{L}}_{i+1}]) - [\overline{\overline{\mathrm{L}}}_i]\} - k_a[\mathrm{L}]\{[\overline{\mathrm{C}}_i]N_{s,i} - [\overline{\mathrm{L}}_i]\} - k_e[\overline{\mathrm{L}}_i] \qquad 3 \le i \le 400 \tag{S18}$$

We solved the equations numerically using ode15s solver in MATLAB. The solution to the equations provides the concentration of clusters with *i* monomers with average concentration of ligands on clusters with *i* monomers in time *t*. We convert the monomeric concentration of clusters to the concentration of clusters having a diameter *D* as described in the main text. Table S1 presents diameter intervals taken from Malvern Zetasizer Nano ZS instrument to create histograms using Eq. S19, S20.

$$\mathrm{C}_{\mathrm{hist}}(t) = \frac{\sum_{D_1<D<D_2} \mathrm{C}_D(t)}{\sum_i \mathrm{C}_D(t)} \qquad \text{S19}$$

$$D_{\mathrm{hist}} = \frac{\sum_{D_1<D<D_2} D\mathrm{C}_D}{\sum_D \mathrm{C}_D(D)} \qquad \text{S20}$$

Table S1. Diameter intervals used in histograms.

D_1 (nm)	D_2 (nm)
0.000	0.400
0.400	0.463
0.463	0.536
0.536	0.621
0.621	0.719

0.719	0.833
0.833	0.965
0.965	1.117

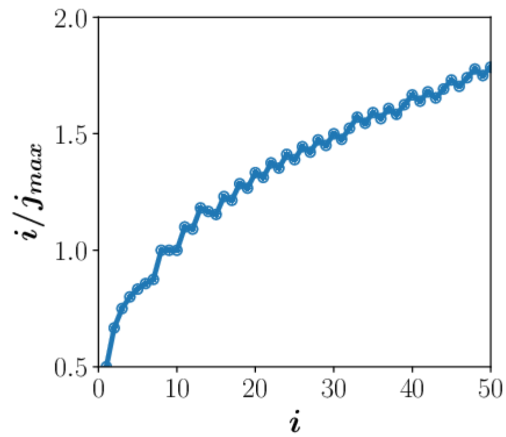

Figure S1: Ratio of metal atoms, i, to the number of ligand binding sites $j_{\max}$ (defined by $N_{s,i}$) as a function of the number of metal atoms in the cluster. As the figure indicates, the ratio increases with i.

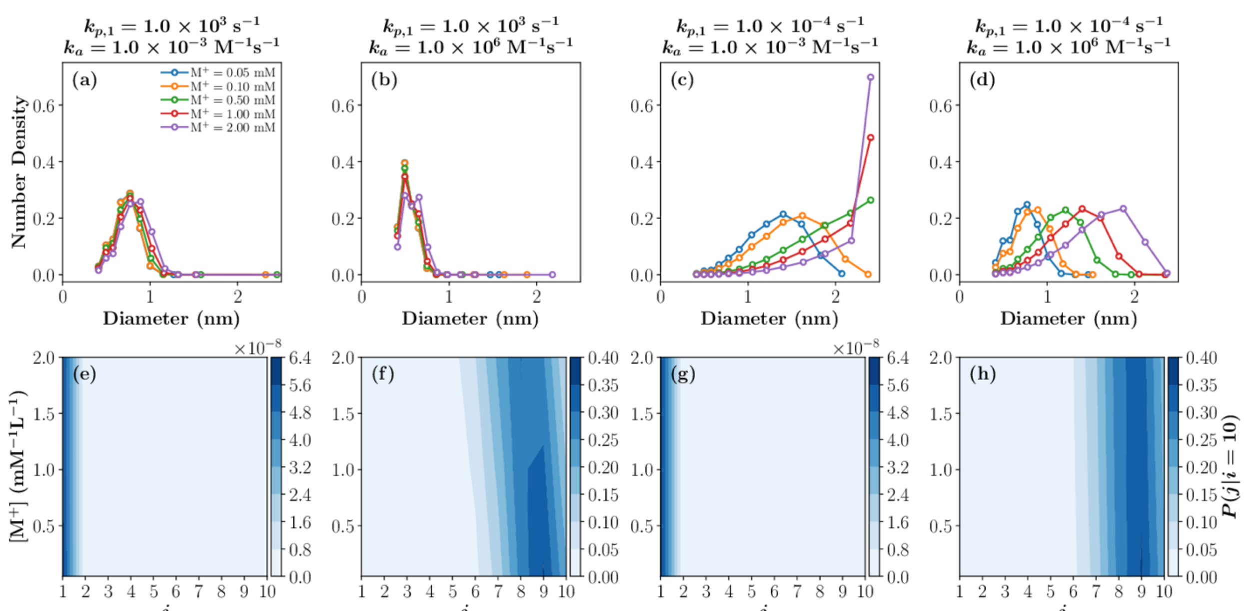

Figure S2: Figure 7 of the manuscript reproduced with a ligand binding rate of $k_b = 10^2$ M^{-1} s^{-1}.

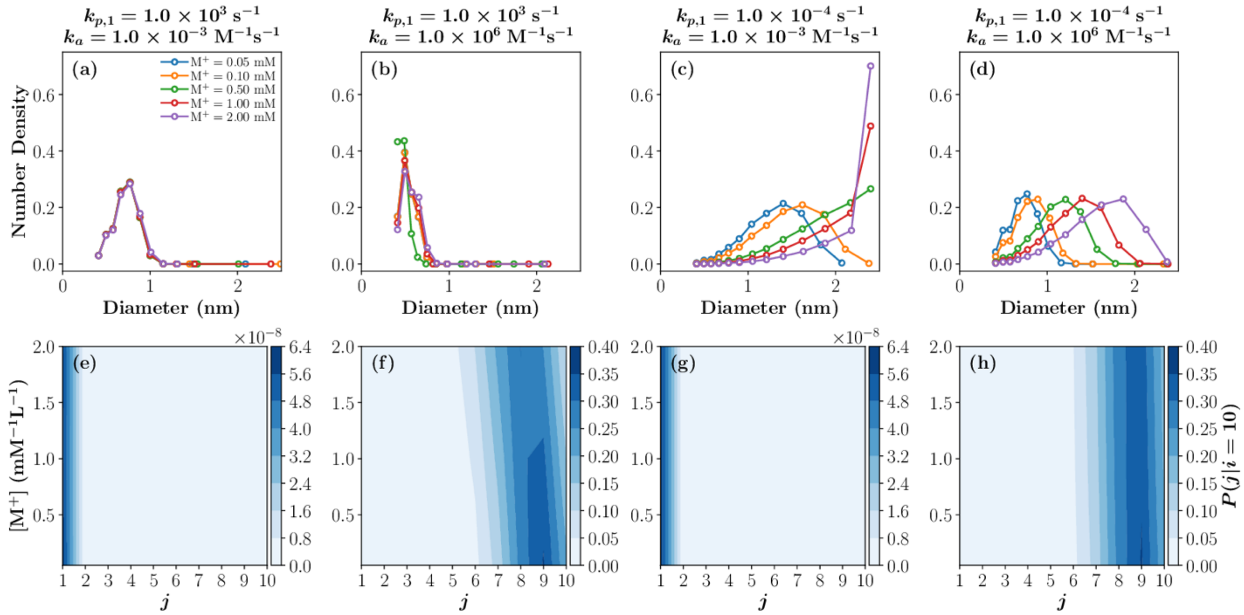

Figure S3: Figure 7 of the manuscript reproduced with a ligand binding rate of $k_b = 10^3$ M^{-1} s^{-1}.

Scheme 4: Reaction scheme for Figure S4 incorporating bare metal growth.

$$\mathrm{M}^{+} \xrightarrow{k_{p,1}} \mathrm{M} \tag{1a}$$

$$\mathrm{M} + \mathrm{L} \xrightleftharpoons[k_{ub,1}]{k_{b,1}} \mathrm{ML} \tag{1b}$$

$$\mathrm{M}^{+} + \mathrm{L} \xrightleftharpoons[k_{ub,2}]{k_{b,2}} \mathrm{ML} \tag{1c}$$

$$\mathrm{ML}^{+} \xrightarrow{k_{p,2}} \mathrm{ML} \tag{1d}$$

$$\mathrm{M} + \mathrm{M} \xrightarrow{k_{n1}} \mathrm{C}_{2,0} \tag{1e}$$

$$\mathrm{ML} + \mathrm{M} \xrightarrow{k_{n2}} \mathrm{C}_{2,1} \tag{1f}$$

$$\mathrm{ML} + \mathrm{M}^{+} \xrightarrow{k_{n3,ac}} \mathrm{C}_{2,1} \tag{1g}$$

$$\mathrm{M} + \mathrm{ML}^{+} \xrightarrow{k_{n4,ac}} \mathrm{C}_{2,1} \tag{1h}$$

$$\mathrm{ML} + \mathrm{ML} \xrightarrow{k_{n}} \mathrm{C}_{2,2} \tag{1i}$$

$$\mathrm{ML} + \mathrm{ML}^{+} \xrightarrow{k_{n,ac}} \mathrm{C}_{2,2} \tag{1j}$$

$$\mathrm{C}_{i,j} + \mathrm{M} \xrightleftharpoons[k_{d1,j}]{k_{g1,i,j}} \mathrm{C}_{i+1,j} \tag{1k}$$

$$\mathrm{C}_{i,j} + \mathrm{M}^{+} \xrightleftharpoons[k_{d2,j,ac}]{k_{g2,i,j,ac}} \mathrm{C}_{i+1,j} \tag{1l}$$

$$\mathrm{C}_{i,j} + \mathrm{ML} \xrightleftharpoons[k_{d,j+1}]{k_{g,i,j}} \mathrm{C}_{i+1,j+1} \tag{1m}$$

$$\mathrm{C}_{i,j} + \mathrm{ML}^{+} \xrightleftharpoons[k_{d,j+1,ac}]{k_{g,i,j,ac}} \mathrm{C}_{i+1,j+1} \tag{1n}$$

$$\mathrm{C}_{i,j} + \mathrm{L} \xrightleftharpoons[k_{e,j+1}]{k_{a,i,j}} \mathrm{C}_{i,j+1} \tag{1o}$$

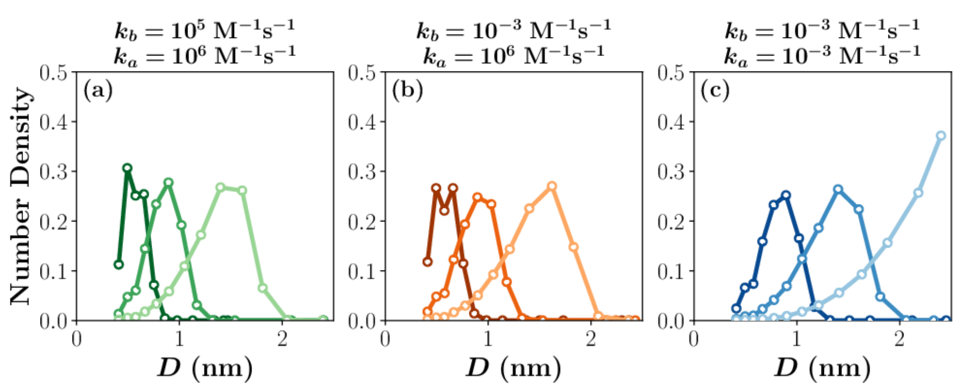

Figure S4: Size distribution for different growth rates (colors) and ligand binding rates: (a) $k_b = 10^5$ M^{-1} s^{-1}, $k_a = 10^6$ M^{-1} s^{-1}, (b) $k_b = 10^{-3}$ M^{-1} s^{-1}, $k_a = 10^6$ M^{-1} s^{-1}, and (c) $k_b = 10^{-3}$ M^{-1} s^{-1}, $k_a = 10^{-3}$ M^{-1} s^{-1}. Dark is $k_g = 10^3$, medium is 10^4, and light is 10^5 M^{-1} s^{-1}. The nanoclusters grow uncontrollably as k_g increases when the ligand binding rates are small (c). The values for the rate coefficients not listed are the same as listed in Table 2, Scheme 3 in the main text.

References

1. Lazzari, S.; Theiler, P.; Shen, Y.; Coley, C.; Stemmer, A.; Jensen, K. Ligand-Mediated Nanocrystal Growth. *Langmuir* **2018**, *34* (10), 3307-3315.