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, \( M^{-1} \ s^{-1} \)

\( k_{g,ac} \)  
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, −
Here we present the rate equations in our model before and after applying method of moments. The reaction scheme is reproduced below:
M⁺ $\xrightarrow{k_{p,1}}$ M ; Monomer formation \hspace{1cm} (S1a)

M + L $\xrightarrow{k_{a,b,1}}$ ML ; Ligand association with metal atom \hspace{1cm} (S1b)

M⁺ + L $\xrightarrow{k_{a,b,2}}$ ML⁺ ; Ligand association with metal ions \hspace{1cm} (S1c)

ML⁺ $\xrightarrow{k_{p,2}}$ ML ; Monomer formation \hspace{1cm} (S1d)

ML + ML $\xrightarrow{k_{ab}}$ C₂₂ ; Self-dimerization \hspace{1cm} (S1e)

ML + ML⁺ $\xrightarrow{k_{ab,2}}$ C₂₂ ; Autocatalytic dimerization \hspace{1cm} (S1f)

Cᵢⱼ + ML $\xrightarrow{k_{e,i,1}}$ Cᵢ₊₁ⱼ₊₁ ; Monomer addition growth \hspace{1cm} (S1g)

Cᵢⱼ + ML⁺ $\xrightarrow{k_{e,i,2}}$ Cᵢ₊₁ⱼ₊₁ ; Autocatalytic growth \hspace{1cm} (S1h)

Cᵢⱼ + L $\xrightarrow{k_{e,i}}$ Cᵢ₊₁ⱼ₊₁ ; Ligand association/elimination to cluster \hspace{1cm} (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:

$$\frac{d[M⁺]}{dt} = k_{p,1}[M⁺] + k_{a,b,1}[M⁺][L] + k_{ab,1}[ML⁺]$$ \hspace{1cm} (S2)

$$\frac{d[M]}{dt} = k_{p,1}[M⁺] + k_{b,1}[M][L] + k_{ab,2}[ML]$$ \hspace{1cm} (S3)

$$\frac{d[L]}{dt} = k_{b,1}[M][L] + k_{ab,1}[ML] + k_{b,2}[M⁺][L] + k_{ab,2}[ML⁺]$$ \hspace{1cm} (S4)

$$\frac{d[ML]}{dt} = k_{p,2}[ML⁺] + k_{b,1}[M][L] + k_{ab,1}[ML] + 2k_{a}[ML]² + k_{n,2}[ML][ML⁺]$$ \hspace{1cm} (S5)

$$k_{a}[ML] [Cᵢⱼ](Nₛᵢ, j) + k_{g} [Cᵢⱼ](Nₛᵢ, j)$$

$$k_{d}[ML] [Cᵢⱼ](Nₛᵢ, j) + k_{d}[Cᵢⱼ](Nₛᵢ, j)$$

$$k_{d}[ML] [Cᵢⱼ](Nₛᵢ, j) + k_{d}[Cᵢⱼ](Nₛᵢ, j)$$
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

\[
\frac{d[M^+]}{dt} = k_{h,2}[M^+][L] + k_{ab,2}[ML^+] + k_{n,ac}[ML][ML^+] \\
\frac{d[M]}{dt} = p_{1}[M^+] + k_{h,2}[M][L] + k_{ab,2}[ML] \\
\frac{d[L]}{dt} = -k_{h,2}[M][L] + k_{ab,1}[ML] - k_{h,2}[M^+][L] + k_{ab,2}[ML^+] \\
\frac{d[ML]}{dt} = k_{p,2}[ML^+] + k_{h,1}[M][L] - k_{ab,1}[ML] - 2k_{n}[ML]^2 - k_{n,ac}[ML][ML^+] \\
\frac{d[ML^+]}{dt} = -k_{p,2}[ML^+] + k_{h,2}[M^+][L] - k_{ab,2}[ML^+] - k_{n,ac}[ML][ML^+] \\
\]

(S6)
\[
\frac{d}{dt}[\bar{C}_2] = k_n[ML]^2 + k_{na,ac}[ML][ML^+] - (k_g[ML] + k_{g,ac}[ML^+])\{[\bar{C}_2]N_{s,2} - [\bar{L}_2]\}
\]
\[
+ (k_d + k_{d,ac})[\bar{L}_3]
\]  
(S14)

\[
\frac{d}{dt}[\bar{L}_2] = k_n[ML]^2 + k_{na,ac}[ML][ML^+] - (k_g[ML] + k_{g,ac}[ML^+])\{[\bar{L}_2]N_{s,2} - [\bar{L}_2]\}
\]
\[
+ (k_d + k_{d,ac})\{[\bar{L}_2] - [\bar{L}_3]\} - k_g[L]\{[\bar{C}_2]N_{s,2} - [\bar{L}_2]\} - k_e[\bar{L}_2]
\]  
(S16)

\[
\frac{d}{dt}[\bar{C}_i] = -(k_g[ML] + k_{g,ac}[ML^+])\{([\bar{C}_i]N_{s,i} - [\bar{L}_i]) - ([\bar{C}_{i-1}]N_{s,i-1} - [\bar{L}_{i-1}])\}
\]
\[
+ (k_d + k_{d,ac})\{[\bar{L}_{i-1}] - [\bar{L}_i]\} \quad 3 \leq i \leq 400
\]  
(S17)

\[
\frac{d}{dt}[\bar{L}_i] = -(k_g[ML] + k_{g,ac}[ML^+])\{([\bar{L}_i]N_{s,i} - [\bar{L}_i]) - ([\bar{C}_{i-1}]N_{s,i-1} + [\bar{L}_{i-1}] + N_{s,i-1} - 1 - [\bar{L}_{i-1}])\}
\]
\[
+ (k_d + k_{d,ac})\{[\bar{L}_{i-1}] - [\bar{L}_i]\} - k_g[L]\{[\bar{C}_i]N_{s,i} - [\bar{L}_i]\} - k_e[\bar{L}_i] \quad 3 \leq i \leq 400
\]  
(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.

\[
C_{\text{hist}}(t) = \frac{\sum_{D_i<\bar{D}<D_{i+1}} C_D(t)}{\sum D_C(t)} \quad \text{S19}
\]

\[
D_{\text{hist}} = \frac{\sum_{D_i<\bar{D}<D_{i+1}} DC_D}{\sum D_C(D)} \quad \text{S20}
\]

<table>
<thead>
<tr>
<th>(D_1) (nm)</th>
<th>(D_2) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.400</td>
</tr>
<tr>
<td>0.400</td>
<td>0.463</td>
</tr>
<tr>
<td>0.463</td>
<td>0.536</td>
</tr>
<tr>
<td>0.536</td>
<td>0.621</td>
</tr>
<tr>
<td>0.621</td>
<td>0.719</td>
</tr>
</tbody>
</table>
**Figure S1:** Ratio of metal atoms, $i$, to the number of ligand binding sites $j_{\text{max}}$ (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$^{-1}$. 

<table>
<thead>
<tr>
<th></th>
<th>0.719</th>
<th>0.833</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.833</td>
<td>0.965</td>
<td></td>
</tr>
<tr>
<td>0.965</td>
<td>1.117</td>
<td></td>
</tr>
</tbody>
</table>
**Figure S3:** Figure 7 of the manuscript reproduced with a ligand binding rate of \(k_b = 10^3 \text{ M}^{-1} \text{s}^{-1}\).

**Scheme 4:** Reaction scheme for Figure S4 incorporating bare metal growth.
Figure S4: Size distribution for different growth rates (colors) and ligand binding rates: (a) $k_g = 10^5 \text{ M}^{-1}\text{s}^{-1}$, $k_a = 10^6 \text{ M}^{-1}\text{s}^{-1}$, (b) $k_g = 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, $k_a = 10^6 \text{ M}^{-1}\text{s}^{-1}$, and (c) $k_g = 10^{-3} \text{ M}^{-1}\text{s}^{-1}$, $k_a = 10^3 \text{ M}^{-1}\text{s}^{-1}$. Dark is $k_g = 10^3$, medium is $10^4$, and light is $10^5 \text{ M}^{-1}\text{s}^{-1}$. 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