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# Host-guest Sensing of Polymer by the Luminescence Enhancement of Silver Nanodots

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## Abstract

# Host-guest Sensing of Polymer by the Luminescence Enhancement of Silver Nanodots

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A clear demonstration of linear polymers showing the most suitable binding to guest counterparts is still unknown. Luminescent polyacrylic acid (PAA) stabilized silver nanodots (PAA-AgNDs) have been applied as turn-on sensors to monitor host-guest interactions between PAA chains and binding cations. The binding of carboxylates of PAA and group 2 cations can cross-link the PAA chain, which increases the rigidity of the PAA chain, slows the non-radiative decay of the PAA-AgNDs, and consequently improves the emission and

induces a blue shift of silver nanodots. Meanwhile, a simple visualization method with acrylamide gel and a simple experiment with several types of water have shown that PAA-silver nanodots can be excellent probes for detecting host-guest interactions between polymer and group 2 cations.

**Keywords:** luminescent silver cluster, polyacrylic acid, host-guest chemistry, group 2 ions, rigidity, spectral shift

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# I. Introduction

#### **1.1 Host-guest chemistry**

#### 1.1.1 What is host-guest chemistry?

Supramolecular chemistry focuses on the properties and intermolecular forces of supramolecules consisting of multiple molecules.<sup>1</sup> The intermolecular forces noted in supramolecular chemistry are noncovalent interactions between molecules, rather than covalent bonds that are mainly concentrated in traditional chemistry.<sup>2</sup> Examples of non-covalent interactions include hydrogen bonding, van der Waals forces, electrostatic attractions, and metal coordination bonds.<sup>3</sup> Supramolecular systems can exhibit reactions by any stimulus because they exist in conjunction with each other by non-covalent interactions. Using these features, supramolecular chemistry has been explored in various fields, including molecular sensors, gas absorption, chemical catalysts, and drug delivery.<sup>4</sup>

Host-guest chemistry is a branch of supramolecular chemistry in which host molecules bind guest molecules or ions. Host-guest interactions describe complexes consisting of two molecules or ions that have unique structural properties or can make non-covalent bonds in supramolecular chemistry.<sup>5</sup> The components of host-guest interactions are usually host molecules with structures capable of capturing other molecules and guest molecules smaller than host molecules and capable of binding to host.

#### $Host + Guest \rightleftharpoons Host - guest complex$

Various types of host molecules include cyclodextrins, urea, cyclotriphosphazines, crown ether, and so on.<sup>6, 7</sup> These host molecules can recognize and bind to certain guest molecules, such as small molecules or ions, and in this way, the bonding between the host and the guest can be said to be selective.<sup>8</sup> By this feature, host-guest interactions are also called molecular recognitions. Avidin, which shows a very high affinity for biotin, is one of the examples of host-guest interactions. It is also well known that the crown ether of the ring-shaped structure combines with several metal cations to form a hostguest complex.<sup>9, 10</sup>

#### 1.1.2 Applications of host-guest chemistry

Host-guest interactions play a particularly important role in molecular sensing using molecular recognition properties and self-assembly.<sup>11, 12</sup> The meaning of the sensor using host-quest interactions can be interpreted as using a series of characteristics that are active or inactive during the formation of host-guest complex. A well-defined host-guest system can be applied as an ideal platform for studying and controlling specific interactions between biomolecules such as proteins. Beneficial applications of combinations of protein with host-quest chemistry include bio-nanotechnology fields such as biosensors.<sup>13</sup> More specific biomedical applications include drug delivery, gene delivery, bioimaging, and photodynamic therapy.<sup>14</sup> Especially, host-guest complexes between macrocyclic molecules and fluorescent dyes exhibit fluorescence in response to stimuli and can be used for bioimaging. It is used not only in biological applications, but also in approaches to information encryption using host-guest interactions.<sup>15</sup> Consequently, applications using host-guest interactions are being studied in many research fields. Researchers are making efforts to design more complex and potentially applicable host molecules t

hat match the properties of a particular guest molecule.<sup>16, 17</sup>

#### 1.2 What is silver nanodots?

#### 1.2.1 Silver nanodots

Many materials have new properties that we did not originally see when their particle size changes from bulk to nanoscale. Metal silver exhibits different luminescent properties between bulk silver, silver nanoparticle, and several silver atoms, which brilliantly demonstrate that particle size affects the properties of the materials.<sup>18</sup> Silver nanodots (AgNDs) are few-atom clusters of reduced silver atoms that exhibit good luminescent photophysical properties including high quantum yields, good extinction coefficient, excellent photostability, short luminescent lifetime, and excellent two photon absorption cross section.<sup>19</sup> Surface plasmon resonance (SPR) causes conduction electrons on the metal surface to oscillate when silver nanoparticles are irradiated by a specific light source. So, silver nanoparticles can absorb the light but cannot show emission. However, silver nanodots can show not only strong absorption of the light but also bright luminescence<sup>20, 21</sup>

Various scaffolds protecting silver nanodots have been studied due to

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vulnerable properties of unprotected silver nanodots, such as the risk of oxidation by their surroundings and aggregation into larger nanoparticles.<sup>22, 23</sup> As a specific example, synthetic polymers such as poly acrylic acid, single-stranded DNA, and peptides/proteins are widely used as protection group of silver nanodots<sup>19, 24, 25</sup> Depending on the protection group of silver nanodots, the emission wavelength and emission intensity represented by silver nanodot vary.

#### 1.2.2 Applications of silver nanodots

The photophysical properties and photostability of silver nanodots can be varied by the interactions of the protection group with the surrounding environment. There are many studies that utilize silver nanodots as sensors using emission enhancement or quenching when protection group of silver nanodots interacts with surrounding materials.<sup>19, 26, 27</sup> Silver nanodots are also used in luminescence molecular imaging fields such as cellular staining by taking advantage of the excellent photopysical properties and biocompatibility of silver nanodots.<sup>19, 24, 28</sup> Not only the biological applications of silver nanodots,

the size of nanocage can be measured using silver nanodots by the Förster resonance energy transfer (FRET) between the FRET pair of silver nanodots.<sup>29</sup>

#### **1.3 Host guest sensing of PAA-AgNDs with cations**

Unlike proteins, linear polymers act only as host molecules when they contain host-like binding groups in order to form a polymer super host-guest matrix.<sup>30</sup> Simple linear polymers may not function as good hosts because there were no reports on this topic. However, theoretically, there must be linear polymer chain selectivity towards its binding sites. Such changes in their affinity can significantly alter polymer/biomolecular conformation, resulting in changes in stability and functionality such as molecular recognition in biomineralization.<sup>31-</sup> <sup>33</sup> Regarding the interaction between cations and macromolecule, such as organic mineralization, we may have interesting questions about why calcium is the most abundant mineral in the human body.<sup>34</sup> So, we need to understand how cations react specifically with linear polymers. Researches have been reported on the specific binding of various polymers to metals<sup>35, 36</sup>, but research reports on host-guest interactions, in which simple linear polymers become host molecules and selectively recognize specific guest molecules, are still unknown. Therefore, in this study, we can explore the host (polymer)-guest (cations) selectivity that leads to a complex between PAA and a specific metal

cation using linear polymer chain, a polyacrylic acid (PAA) with multi-carboxylic acid functional groups.

Various analytical methods, such as nuclear magnetic resonance (NMR), calorimetry, UV-Vis spectrophotometry, potentiometric titrations and isothermal titration have been used to monitor the host-guest interactions.<sup>37-41</sup> Although photoluminescent signals can be used to monitor the binding between polymer and cations, most studies have used the quenching of photoluminescence with the binding. This indicates the need for research on a photoluminescent sensor that monitors the interaction between polymer and cations using a turn-on strategy.<sup>42, 43</sup> In particular, we could effectively observe the interaction between polymer and cations in this work using the photophysical properties of PAA-stabilized silver nanodots, which are enhanced in the binding of certain group 2 metal cations to PAA.

Luminescent silver nanodots are protected by protection groups such as peptide, single-stranded DNA, and polymer, showing a variety of excellent photophysical properties.<sup>19, 44</sup> These photophysical properties such as emission intensity and emission wavelength can change as the protection group of silver nanodots interacts sensitively with surrounding environment.<sup>19, 24, 25, 27, 45</sup> The

linear polyacrylic acid is a good protection group that can create stable silver nanodots, and it has the advantage of being inexpensive compared to peptide and single-stranded DNA, and it is not difficult to make.<sup>24, 44, 46-48</sup> Thus, PAA-stabilized silver nanodots can be utilized to detect the interaction between the PAA polymer chain and the binding cations.

## **II.** Experimental section

#### 2.1. Materials

Poly acrylic acid (MW~1.8 kDa) (PAA), silver nitrate (99.9999%), 3-(2-amino ethyl amino) propyl dimethoxy methyl silane, anhydrous methanol, sodium hydroxide, sodium borohydride, calcium nitrate tetrahydrate, strontium nitrate, magnesium nitrate hexahydrate, magnesium sulfate heptahydrate, barium nitrate, aluminum sulfate hexadecahydrate, potassium chloride, copper sulfate pentahydrate, gold(III) chloride trihydrate, potassium ferricyanide(III), zinc nitrate hexahydrate, glycerol, poly(ethyleneimine) solution, N,N,N',N'-tetramethylethylenediamine, poly acrylic acid sodium salt solution(MW~8kDa) and ammonium persulfate were purchased from Sigma-Aldrich and used as received. Deionized water (DIW) was obtained on a Millipore Direct-Q 3 ultrapure water system with a resistivity of  $18.2 \text{ M}\Omega$  cm. Acrylamide (40%)/Bis solution 19:1 was purchased from Bio-rad.

#### 2.2. Instruments

Emission and excitation spectra were obtained on a PTI QuantaMasterTM 40 fluorimeter. Absorption spectra were obtained on a Sinco S-4100. pH was adjusted on a Eutech, SG/PH510 pH meter. Lifetime data was obtained on an EasyLife™ X Filter Fluorescence Lifetime Fluorometer with a 470 nm LED pulse light source and a 545–580 nm bandpass emission filter. An Ilshin ® Freeze dryer was used for freeze-drying of samples. Fourier-transform infrared spectroscopy (FTIR) was obtained on Bruker VERTEX80v FTIR spectrometer.

#### 2.3. Preparation and measurement of samples

#### 2.3.1. Synthesis of poly acrylic acid-stabilized AgNDs

Silver-silane stock solution (14 mM) was prepared by mixing silver nitrate (12 mg) and 3-(2-aminoethylamino) propyldimethoxymethylsilane at an amino silane/Ag+ ratio of two in anhydrous methanol (5 mL) for 2 hrs. PAA stock solution (1.8 KDa, 10  $\mu$ L of 8.1 mM pH 8) was added into DIW (968  $\mu$ L),

followed by the addition of silver-silane solution (17  $\mu$ L) with a final ratio of 1:2 of silver and silane and 1:3 of polymer and silver. The mixture was then reduced with fresh sodium borohydride stock solution (4.60  $\mu$ L, 52.87 mM) and stirred overnight in the dark. For preparing PAA-AgNDs with high molecules weight of PAA sodium salt solution, PAA stock solution (8 KDa, 3  $\mu$ L of 8.1 mM pH 8) was added into DIW (975  $\mu$ L), followed by the addition of silver-silane solution (17  $\mu$ L). The mixture was then reduced with fresh sodium borohydride stock solution (4.60  $\mu$ L, 52.87 mM) and stirred overnight in the dark.

# 2.3.2. Observation of emission enhancement of PAA-AgNDs with various cation

PAA-AgNDs (500  $\mu$ L) was mixed with each concentration of various cationic aqueous solution (500  $\mu$ L) and the emission and absorption of the mixture were measured immediately.

#### 2.3.3. Polyacrylamide gel formation

Acrylamide (40%)/Bis solution 19:1 (2.5 mL) was mixed with 30.8 mL of DIW. Twenty microliters of TEMED (N,N,N',N'-tetramethylethylenediamine) was added into acrylamide/bis solution mixture and vortexed. Lastly, 100  $\mu$ L of 10% ammonium persulfate was added into the mixture with constant vortexing. After adding ammonium persulfate, the mixture must be quickly poured into a petri dish within a few seconds to prevent gel formation in the conical tube. The gel was freeze-dried with a freeze-dryer, and then used in the experiment.

## **III.** Results and Discussion

# 3.1. Photophysical properties of PAA-AgNDs with various cations and charged polymer



**Figure 1.** A) Fully scanned emission spectra of PAA-AgNDs with varied excitation wavelengths in deionized water. B) Excitation (monitored at 645 nm, black) and emission spectra (excited at 530 nm, red) of PAA-AgNDs. PAA-AgNDs concentration: 40 µM based on PAA. 'Ex@xxx nm' stands for emission spectrum excited at xxx nm.

As shown in Figure 1A, the emission spectra of PAA-stabilized silver nanodots showed multiple peaks that could be attributed to various non-

specifically generated silver nanodots under polymer protection, as indicated by a full scan of emission spectra of various excitation wavelengths. However, the main species had a maximum emission wavelength of 645 nm with the peak of the excitation spectrum peaked at 530 nm (Figure 1B). The interaction between PAA-AgNDs and ions has not been fully investigated. To the best of our knowledge, the only report on the reaction of luminescent PAA-AgNDs to ions was the extinction of luminescence by chloride due to the formation of silver chloride.49, 50 For the first time, we observed significantly enhanced emissions of PAA-AqNDs in the presence of ions. Through this study, we found that PAA-AgNDs showed significant luminescence enhancements, especially by interacting with group 2 cations. Emission of PAA-AgNDs generally tended to rise in proportion as the concentration of cations added to PAA-AgNDs increased within a specific concentration range of cations. The reactions of various metal cations and PAA-AqNDs, the noticeable results of the group 2 cations, and the applications of research results will be described sequentially.



#### 3.1.1 Interaction of PAA-AgNDs with various cations

**Figure 2.** The degree of emission enhancement when PAA-AgNDs and various cations are mixed. Luminescence was measured immediately after mixing PAA-AgNDs and cations. The total concentration of the cation is A)0.25 mM, B)2.5 mM, C)25 mM and D)250 mM. As the concentration of cations increases, there is no increase in emission in cations other than group 2 elements. The increase in emission of group 2 elements was in the order of calcium, strontium, barium, and magnesium in all concentration areas except 250 mM. D) Due to the solubility problem at high concentrations, several cations were excluded

from the results.

**Figure 2** shows how luminescence enhancement appears when various metal cations are added to PAA-AgNDs. It can be seen that the emission improvement of PAA-AgNDs increases or remains at a certain level as the concentration of the group 2 cation increases. On the other hand, cations other than the group 2 cation did not clearly show emission improvement as the concentration of cation increased. In particular, zinc and cadmium ions interacted with PAA-AgNDs at low concentrations of about 0.25 mM to improve emission, but unlike group 2 cations, they did not show a consistent emission improvement as the concentration of cation of cations at low concentrations of about 0.25 mM to improve emission, but unlike group 2 cations, they did not show a consistent emission improvement as the concentration of cations increased.



**Figure 3.** Comparison of emission enhancement of PAA-AgNDs with calcium(black) and cadmium(red) cation.

**Figure 3** shows how calcium ions and cadmium ions react differently from PAA-AgNDs at concentrations near 0.25 mM. At low concentrations, emission improvement of both types of ions steadily increases, but in the case of cadmium ions, it can be seen that the emission of PAA-AgNDs was decreased rapidly near the concentration of 0.3 mM. Another notable difference is that the degree of emission enhancement is higher in calcium. From these results, we can clearly see that the group 2 cations interact uniquely with PAA-AgNDs. Therefore, it is necessary to examine in more detail how it reacts with PAA-AgNDs depending on the type of group 2 cations.



3.1.2 Interaction of PAA-AgNDs with group 2 cations

Figure 4. Spectral shift of PAA-AgNDs in the presence of calcium ions. A) Fully

scanned emission spectra of PAA-AgNDs in the presence of 1.7 mM calcium

ions. B) Absorption spectra of PAA-AgNDs in the absence (black) or presence (cyan) of 1.7 mM calcium ions.

When calcium ions (1.7 mM) were added into the above PAA-AgND solution, its maximum emission intensity increased almost three-fold with an obvious blue shift of the emission peak from 645 nm (**Figure 1A**) to 602 nm (**Figure 4A**). This blue shift was also reflected in its absorption spectrum (**Figure 4B** cyan line).

A detailed study of calcium ion dependence is shown in **Figure 5**. Calcium ion dependence is shown by plotting the ion concentration to the ratio of PAA-AgNDs emission intensity at a given Ca<sup>2+</sup> concentration to control. At a fixed excitation wavelength of 530 nm, the emission intensity of PAA-AgNDs increased linearly as the calcium ion concentration increased before it leveled off above 0.15 mM of [Ca<sup>2+</sup>] (**Figure 5A and 5B**). As shown in **Figure 1**, the maximum emission intensity of the PAA-AgNDs itself appears at an emission wavelength of about 645 nm when the excitation wavelength is 530 nm. When calcium ions of about 0.2 mM or more reacted with PAA-AgNDs, the excitation wavelength with this maximum emission intensity changed, and the emission

wavelength also shifted further to blue. At high calcium concentrations, the emission wavelength of PAA-AgNDs was blue shifted to 610 nm (**Figure 5D**). There was a significant change in the spectrum in **Figure 5C**, which obtained emission spectra at two different excitation wavelengths (530 nm and 500 nm).

This emission enhancement of PAA-AgNDs by calcium ions exceeded general expectations that silver and cations may compete for PAA when general cations are added to PAA-AgNDs. PAA is believed to bind silver species much weaker than other silver stabilizing groups such as DNA bases.<sup>24</sup> As a result, any cations may compete with silver species at the binding site of PAA chains to destabilize silver nanodots with quenching of silver nanodots. However, calcium ions did not replace silver species in the PAA chain, probably because silver species exhibit stronger binding affinity to PAA chains than calcium ions. Surprisingly, emission enhancements of PAA-AgNDs indicated that calcium ions interact with PAA chains.



depended on the concentration of calcium. A) Emission intensity of PAA-AgNDs with calcium (0-0.50 mM) excited at 530 nm. B) Emission enhancement of PAA-AgNDs depended on the concentration of calcium. C) Maximum value of emission intensity of PAA-AgNDs with calcium (0-0.50 mM). Excitation wavelength is 530 nm from control to 0.25 mM of calcium and 500 nm from 0.30 mM to 0.50 mM of calcium. D) Emission wavelength of PAA-AgNDs depended on the concentration of calcium. The result of the value measured by fixing the excitation wavelength to 530 nm (**•**) and the highest value among

the total emission (•). The error bar indicates the standard error.

Among the mechanisms for enhancement of emission intensity, restricting the non-radiative decay of excited states of molecules may be most likely in our research.<sup>51-54</sup> This means that PAA-AgNDs will be sensitive to environmental viscosity and temperature. Moving PAA-AqNDs to an aqueous glycerol solution (80% (v/v)) caused to be increased their emission intensity two times with its maximum emission peak also shifted to 628 nm (Figure 6A). Temperature showed a stronger effect on the PAA-AqNDs spectrum. As shown in Figure 6B, the temperature of the PAA-AgNDs solution was adjusted from 50 °C to -80 °C, and the emission strength increased by six times. The maximum emission peak was also shifted to 658 nm at 50 °C and 615 nm at 80 °C. Both low temperature and high viscosity slowed the vibrational deactivation of excited PAA-AgNDs and increased emission intensity.<sup>55</sup> Furthermore, when the temperature is low and the viscosity is high, the solvation speed of the silver nanodots is also slowed, thereby increasing the contribution from the high energy vibration energy level to the steady-state spectrum, resulting in a blue shift of the steadystate spectrum at low temperatures.<sup>56, 57</sup>

![](_page_30_Figure_0.jpeg)

**Figure 6.** Influence of viscosity and temperature on the spectrum of PAA-AgNDs. Emission intensity ( $\blacksquare$ ) and maximum emission peak ( $\blacktriangle$ ) shift along with the concentration of glycerol (v/v) (A) and temperature (B). Data points were connected with B-spline to show a clear trend of the curve.

We confirmed the binding of calcium ions to PAA chains through Fouriertransform infrared spectroscopy (FTIR) studies. A typical asymmetric stretching band of a carbonyl group in polyacrylic acid is 1717 cm<sup>-1</sup>, but when the polyacrylic acid is deprotonated, the movement of the carbonyl band to low energy is observed where the bond strength of the carbonyl group is weakened by the formation of conjugated –COO<sup>-,58, 59</sup> Since the pH of PAA-AgNDs was about 8, the infrared spectrum of PAA-AgNDs showed a peak similar to that of deprotonated PAA, where carboxylate should be major species with asymmetric vibration bands of 1570 cm<sup>-1</sup> and symmetrical vibration bands of 1337 cm<sup>-1</sup> (**Figure 7A**). According to a report that calcium ions cause infrared spectral shift of carboxylic acid when calcium ions (1.7 mM) are added, the vibration bands moved to low energy to 1562 cm<sup>-1</sup> and 1321 cm<sup>-1</sup> respectively (**Figure 7B**).<sup>60</sup>

![](_page_31_Figure_1.jpeg)

**Figure 7.** Infrared spectra of PAA-AgNDs in the presence of calcium ions. Lyophilized PAA-AgNDs in the absence (A) and presence (B) of 1.7 mM calcium ions were examined on a Bruker FTIR spectrometer.

The calcium ions can cross-link the PAA chains by coordination with carboxylic acids, and increase rigidity of polymer chains, slow the non-radioactive decay, and consequently increase emission intensity of silver nanodots (**Scheme 1**).

![](_page_32_Figure_1.jpeg)

**Scheme 1.** Schematic cartoon showing the binding of calcium ions to a PAA polymer chain. Cross-links between carboxylic acids by the calcium ion (pink) increase the rigidity of the polymer chain, and consequently enhances the photoluminescence of silver nanodots (yellow) and induce the blue shift of its emission spectrum. The sizes of silver and calcium were purposely enlarged. Note that the real structure of the polymer-silver-calcium complex is still unknown. The picture was drawn by Chem3D after minimizing its energy by the MM2 force field method.

![](_page_33_Figure_0.jpeg)

**Figure 8.** Influence of various cations on the emission of PAA-AgNDs. Normalized emission enhancement of PAA-AgNDs by magnesium (black), calcium (red), strontium (green), and barium (blue). Data are presented as mean values+/-SD. N=6 independent technical replicate experiments were done. Each curve was subtracted by 1, and then fitted with modified Equation 9 ( $R_{obs} - 1$ ). The fitting line was shown in the same color as the curve.

A simple model has been developed to evaluate the binding affinity of the polymer for cations from a previous report.<sup>61</sup> In this model, we assumed that the emission intensity and peak wavelength was a composite average of multiple silver species. Given that the PAA chain has multiple guest binding sites (n), and it is not likely to purify each complex with discrete binding number

of guest ions, an overall equilibrium constant (K) was proposed for the PAAbased host-guest systems as in **Eq. 1** 

$$[PAA] + n[Guest] \stackrel{K}{\leftrightarrow} [PAA - n(Guest)] (1)$$

in which each binding site has similar affinity for the guest with minimum interference between each binding site. The binding constant (K) of the above interactions can be described by **Eq. 2** 

$$K = \frac{[PAA - n(Guest)]}{[PAA]_{f}[Guest]_{f}}$$
(2)

where  $[PAA]_{f}$ ,  $[Guest]_{f}$ , and [PAA - n(Guest)] are the molar concentrations of free-state binding sites on PAA, free-state guest, and PAA–guest complex, respectively. In this host-guest system, the material balance of reactants follows the relationship in **Eq. 3**:

 $[Guest]_o = [Guest]_b + [Guest]_f$ 

 $n[PAA]_0 = [Binding site]_f + [Guest]_b$  (3)

where  $[PAA]_o$ ,  $[Guest]_o$  and  $[Guest]_b$  are the initial concentrations of PAA and guest, and the concentration of bound-state guest, respectively.  $[Binding site]_f$  is the concentration of free binding site in each PAA. Thus the molar fraction of bound-state PAA ( $P_b$ ) can be defined by **Eq. 4**:

$$P_{\rm b} = \frac{[{\rm Guest}]_{\rm b}}{n[{\rm PAA}]_{\rm o}} \quad (4)$$

Therefore, *K* can be described by **Eq. 5**:

$$K = \frac{nP_{b}[PAA]_{o}}{([Guest]_{o} - nP_{b}[PAA]_{o})(1 - P_{b})_{n}[PAA]_{o}}$$
(5)

Note that the observed emission enhancement is a combined emission intensity from the free PAA-AgNDs and bound PAA-AgNDs. The enhancement ratio (emission intensity of PAA-AgNDs at a given guest concentration to the control (free of guest)) can be defined by **Eq. 6**:

$$R_b = \frac{I_b}{I_o} \quad (6)$$

where  $I_b$  and  $I_o$  are the emission intensities of PAA-AgNDs in the presence and absence of guest ions, respectively. Thus, the observed enhancement ratio ( $R_{obs}$ ) can be described by **Eq. 7**:

$$R_{obs} = P_b R_b + P_f R_f = P_b R_b + (1 - P_b) R_f$$
 (7)

where  $P_{\rm b}$  and  $P_{\rm f}$  are molar fractions of bound- and free-state, respectively;  $R_{\rm b}$  and  $R_{\rm f}$  are the emission intensity enhancement ratios of the bound- and free-state, respectively. Note that  $R_{\rm b}$  is the maximum enhance ratio  $R_{\rm max}$ , and  $R_{\rm f}$  is actually 1. Therefore, the above equation becomes the following:  $R_{\rm obs} = P_{\rm b}(R_{\rm max} - 1) + 1$  (8)

 $P_{\rm b}$  can be obtained from **Eq. 5**, and **Eq. 8** can be transformed to **Eq. 9** to show the relationship between the emission intensity enhancement ratio  $R_{\rm obs}$  of PAA-AgNDs and binding parameters of the interaction:

$$R_{obs} = \frac{(R_{max} - 1)}{2} \left\{ \left( 1 + \frac{1}{nK[PAA]_o} + \frac{[Guest]_o}{n[PAA]_o} \right) - \left[ \left( 1 + \frac{1}{nK[PAA]_o} + \frac{[Guest]_o}{n[PAA]_o} \right)^2 - \frac{4[Guest]_o}{n[PAA]_o} \right]^{1/2} \right\} + 1 \quad (9)$$

In the equation, we kept the PAA concentration and the guest cations, such as calcium or strontium ions, as independent variables. With different cations, ratios of the emission intensity of PAA-AgNDs at a given cation concentration to the control were plotted versus cation concentration. The curves were then fitted with **Eq. 9**, and the results were shown on **Table 1**. This shows that the calcium ions exhibited the strongest binding affinity for the polymer chain with an equilibrium constant of 780, followed by strontium (400) and barium ions (380), and magnesium ions showed the weakest binding affinity (60, **Figure 8**). The best match of calcium ions in Group 2 to the PAA chain is reminiscent of the characteristics of host-guest chemistry. The polymer chain may be crosslinked to form inter-segment bridges, and consequently raise the rigidity of the polymer chain. In this, the size of cations in the PAA-AqNDs might be a key player. Theoretically, the highest electronegativity of magnesium (1.31) should bring multiple carboxylate groups towards itself to form strong coordinate bonds, and thus induce the highest rigidity. In contrast, the calcium with an electronegativity of 1.00 caused the strongest cross-linking of the polymer chain, which suggests that a larger size of calcium ion ( $Ca^{2+}$ , 114 pm) could better fit the gap between two segments of the polymer chain. Strontium presents a similar electronegativity (0.95) as calcium but a larger size (Sr<sup>2+</sup>, 132 pm), but its binding capability was weaker than calcium ions, likely because it is too large to fit the gap, resulting in loose contact between chelating groups and cations. We also compared  $Cd^{2+}$  with  $Ca^{2+}$  in which both show similar sizes, but  $Cd^{2+}$  exhibits a larger electronegativity (1.69). The results showed that  $Cd^{2+}$ quenched the emission of silver nanodots much more seriously as the concentration of Cd<sup>2+</sup> was increased, suggesting that Cd<sup>2+</sup> replaced silver ions from the PAA chain. (Figure 2, 3)

From our model, we also found that about four to six cations were bound to the polymer chain of PAA-AgNDs. The polymer shows lower affinity for calcium compared to calcium-selective proteins (calmodulin), in which cation-binding amino acid residues such as aspartate, glutamate, and asparagine are finely tuned to form the calcium binding domains, resulting in a binding constant for  $Ca^{2+}$  of up to  $7.0 \times 10^{5.33,62}$  Even though the simple polymer lacks the selectivity toward a specific ion, our study shows that it binds to cations with moderate selectivity. This is important in terms of salt influence on the polymer/protein properties. For example, complexation between calcium ions and carboxylates on a polymer chain suppresses hydrogen-bonding among the moieties in the polymer, and subsequently influences the hydrogen-bonding network and the mechanical properties of the polymer.<sup>63</sup> Our research may also hint why calcium is naturally selected as the richest components in the biomineralization.<sup>64</sup>

	Electronegativity	lon radius	Binding	Equilibrium
	Pauling scale	(pm)	sites	constant
Mg <sup>2+</sup>	1.31	86	5.6 ± 0.6	60 ± 15
Ca <sup>2+</sup>	1.00	114	3.7 ± 0.2	780 ± 60
Sr <sup>2+</sup>	0.95	132	6.0 ± 0.1	400 ± 40
Ba <sup>2+</sup>	0.89	149	6.2 ± 0.3	380 ± 70

**Table 1.** Binding parameters of cations to the PAA polymer.

The luminescent lifetime measurement of PAA-AgNDs (**Figure 9**) also showed the formation of a rigid polymer complex between calcium cations and PAA. With the addition of calcium ions, the lifetime of PAA-AgNDs increased from 0.2 ns to 1.3 ns, increasing in line with the trend of life in a more rigid environment.

![](_page_39_Figure_1.jpeg)

**Figure 9.** Luminescence lifetime of PAA-AgNDs with increasing calcium cation concentration.

The PAA-AgNDs we used in this study used PAA with an average molecular weight of 1.8 kDa. However, PAA-AgNDs could be successfully made with a larger average molecular weight of PAA (8 kDa), and a detailed protocol was described in **experimental section 2.3.1**. A series of experiments were

conducted equally to find out how PAA-AgNDs with large molecular weight PAA interact with calcium ions. Through the results of **Figure 10**, it was possible to observe the same emission enhancement and blue shift of PAA-AgNDs when calcium ions were added regardless of the molecular weight of PAA.

![](_page_40_Figure_1.jpeg)

**Figure 10.** Emission enhancement and spectral blue shift of PAA-AgNDs with high molecular weight PAA also depended on the concentration of calcium. A) Emission enhancement of PAA-AgNDs (with high Mw PAA) depended on the concentration of calcium. B) Emission wavelength of PAA-AgNDs (with high Mw PAA) depended on the concentration of calcium. The result of the value measured by fixing the excitation wavelength to 530 nm (**■**) and the highest value among the total emission (**●**). The error bar indicates the standard error.

#### 3.1.3 Interaction of PAA-AgNDs with charged polymer

In addition to cation, positively charged polymers such as polyethylenimine (PEI) are firmly bonded to the PAA through electrostatic interaction. At low concentrations, the bonds between PAA and PEI increased the rigidity of PAA polymer chains and emission intensity of silver nanodots was increased. But as PEI concentrations continued to increase, emission quenching started as the bond weakened the stability of the silver nanodot.

![](_page_41_Figure_2.jpeg)

**Figure 11.** Emission enhancement(A) and emission wavelength(B) of PAA-AgNDs with polyethyleneimine(PEI). PEI is one of positive charged polymer. The error bar indicates the standard error.

Looking at Figure 11A, the degree of improvement in luminescence increases

until the concentration of PEI is about 15 mM, and then decreases. On the other hand, as shown in **Figure 11B**, the emission wavelength continued to be shortened regardless of the concentration. Looking at the results of the experiment, it can be interpreted that when PEI with positive charge is added to the negatively charged PAA, the rigidity of PAA-AgNDs becomes stronger due to electrostatic reaction, and luminescence is improved to some extent, and emission wavelength is shortened. Compared to metal cations, PEI is a polymer, so there is a difference in molecular weight, so it can be interpreted that the addition of polymers above a certain concentration had a negative effect on the emission of PAA-AgNDs. The tendency to decrease emission wavelength is very similar to the result of the addition of metal cations.

# 3.2 Applications of emission enhancement of PAA-AgNDs with cations

Based on the previous experimental results, it was confirmed that PAA-AgNDs reacts with group 2 metal cations to improve luminescence and cause emission wavelength to be blue-shifted. It is expected that this specific phenomenon can be applied to the field of distinguishing group 2 cations. Polyacrylamide gel experiments, in which luminescence improvement can be seen, were conducted to confirm the difference between group 2 cations and other metal cations using PAA-AgNDs. Furthermore, various types of water were reacted with PAA-AgNDs to confirm the emission enhancement and spectral shift of group 2 cations contained in the water.

![](_page_44_Figure_0.jpeg)

#### 3.2.1 Applications with polyacrylamide gel

**Figure 12.** Luminescence observed under UV lamp (365 nm). A) Control by dropping 1  $\mu$ L of highly concentrated PAA-AgNDs into an Acrylamide gel. B) Luminescence observed immediately after dropping 1  $\mu$ L of each concentration of cationic aqueous solution into the control(A). At 50 and 100 mM, calcium and strontium were observed to have a marked emission increase, and zinc and copper were quenched.

After mixing concentrated PAA-AgNDs with metal cations in a 1:1 ratio, the results observed under UV lamp (365 nm) showed that group 2 cations such as calcium and magnesium brightened the emission of silver nanodots on polyacrylamide gel. Emission remains at low concentrations of zinc and copper,

but emission could no longer be seen at high concentrations. This result is consistent with the experimental results of mixing PAA-AgNDs with metal cations in the results of 3.1.1.

![](_page_45_Figure_1.jpeg)

**Figure 13.** Emission intensity ( $\blacksquare$ ) and emission peaks ( $\blacktriangle$ ) of the PAA-AgNDs in polyacrylamide gel. The spectra of gel with calcium ions were measured on a fluorometer. Data points were connected with B-spline to show a clear trend of the curve.

The reaction between PAA-AgNDs and calcium cations in acrylamide gel was confirmed to be the same as the reaction results on solution. As shown in the results of 3.1.2, the higher the concentration of calcium cations to be added, the greater the luminescence and the shorter the emission wavelength.

![](_page_46_Picture_0.jpeg)

**Figure 14.** Luminescence observed under UV lamp (A-D : 254 nm, E-F : 365 nm). A, E) Control by dropping 100 µL of highly concentrated PAA-AgNDs into an acrylamide gel. B, F) Luminescence observed immediately after dropping 50 mM calcium cationic aqueous solution on the top of control(A). C, G) Observed 7days later. D, H) Observed 28 days later. Scale bar: 1 cm

The patterned acrylamide gel was filled with concentrated PAA-AgNDs, and an aqueous calcium cation solution was applied only to the upper pattern using a brush. Emission was clearly improved only on the side where calcium cation was applied under UV lamp. Through C, D, G, and H of **Figure 14**, it can be seen that the emission of calcium cations lasts longer than that of PAA-AgNDs alone.

#### 3.2.2 Applications with different types of water

In general, tap water contains various cations and anions.<sup>65</sup> Types of cations include calcium, magnesium, sodium, and potassium, and types of anions include chloride and carbonate. Among them, calcium and magnesium are indicators used to indicate water hardness. Hardness of water is largely divided into two categories: soft water and hard water. The WHO defines calcium and magnesium dissolved in a liter of water as light water if they are more than 120 mg, and soft water if they are less than that. The hard water is also called mineral water. Depending on the region, the amount of cation and anion contained in tap water varies. Usually, soft water contains about 0 - 60 mg/L of calcium cation, and hardwater contains 120 -180 mg/L or more. In particular, according to the tap water quality test information provided by the Seoul Metropolitan Government Waterworks Headquarters, the average water hardness of Seoul Metropolitan Government tap water is about 69 mg/L and the average chloride ion content is about 27.8 mg/L as of April 2023.

Water purifiers that people usually use in their daily lives filter tap water through filters to remove various ions and bad substances when drinking. Mineral water sold on the market also varies from low hardness to mineral water containing many minerals.

Calcium and magnesium cations used to represent the hardness of water react with PAA-AgNDs as a group 2 elements to improve luminescence and induce changes in emission wavelength. To confirm this, distilled water, tap water, purification water, and mineral water (Evian) were reacted with PAA-AgNDs respectively to check the results.

![](_page_48_Figure_2.jpeg)

**Figure 15.** The degree of emission enhancement(A) and change of emission wavelength(B) when PAA-AgNDs and different types of water are mixed. Luminescence was measured immediately after mixing PAA-AgNDs and each water type.

As shown in **Figure 15A**, the emission of PAA-AgNDs was improved in other types of water containing calcium and magnesium ions compared to distilled water. Comparing the results of tap water and purification water, as predicted, the hardness of tap water is stronger, so the improvement of emission is also greater. The experiment used Evian mineral water, which belongs to the high hardness side of mineral water to drink. In **Figure 15B**, it can be seen that the emission wavelength was blue-shifted when PAA-AgNDs reacted with various types of water. As in the previous comparison, it was confirmed that the emission wavelength shift in tap water was larger than that of purification water. As such, PAA-AgNDs can be applied to easily check the hardness of water around us or unknown drinks using mineral physical properties that change when reacting with various types of water.

# **IV. Conclusions**

It has been found in this study that the linear polymer chain acts as an open host, showing adequate selectivity for bonding with cations using luminescent silver nanodots. In particular, the combination of the group 2 cations and the polyacrylic acid chain induced emission enhancement and blue shift of the polyacrylic acid stabilized silver nanodots. Given that PAA silver nanodots showed the same results when they were in a viscous and low temperature environment, it can be considered that the binding of the PAA chain to the group 2 cations increased the rigidity of the PAA chain. In conclusion, the combination of the carboxylates of PAA and group 2 cations retards the non-radiative decay of PAA-silver nanodots, resulting in higher emission intensity and induced blue shift of silver nanodots. Furthermore, a simple visualization method with acrylamide gel and a simple experiment with several types of water have shown that PAA-silver nanodots can be excellent probes for detecting host-quest interactions between polymer and group 2 cations.

### V. References

(1) Lehn, J.-M. Supramolecular Chemistry. *Science* 1993, *260* (5115), 1762–1763.
 DOI: doi:10.1126/science.8511582.

(2) Schneider, H.-J. Binding Mechanisms in Supramolecular Complexes. Angew.
Chem.-Int. Edit. 2009, 48 (22), 3924-3977. DOI: https://doi.org/10.1002/anie.200802947.

(3) Biedermann, F.; Schneider, H.-J. Experimental Binding Energies in Supramolecular Complexes. *Chem. Rev.* 2016, *116* (9), 5216-5300. DOI: 10.1021/acs.chemrev.5b00583.

(4) Huang, F.; Anslyn, E. V. Introduction: Supramolecular Chemistry. *Chem. Rev.*2015, *115* (15), 6999–7000. DOI: 10.1021/acs.chemrev.5b00352.

(5) Seyrek, E.; Decher, G. 7.09 - Layer-by-Layer Assembly of Multifunctional Hybrid Materials and Nanoscale Devices. In *Polymer Science: A Comprehensive Reference*, Matyjaszewski, K., Möller, M. Eds.; Elsevier, 2012; pp 159-185.

(6) Mou, Q.; Ma, Y.; Jin, X.; Yan, D.; Zhu, X. Host-guest binding motifs based on hyperbranched polymers. *Chem. Commun.* 2016, *52* (79), 11728-11743, 10.1039/C6CC03643K. DOI: 10.1039/C6CC03643K.

(7) Tonelli, A. E.; Narayanan, G.; Gurarslan, A. Host-Guest Polymer Complexes. *Polymers* 2018, *10* (8), 911. (8) Chernykh, E. V.; Brichkin, S. B. Supramolecular complexes based on cyclodextrins. *High Energy Chemistry* 2010, *44* (2), 83-100. DOI: 10.1134/S0018143910020013.

(9) Livnah, O.; Bayer, E. A.; Wilchek, M.; Sussman, J. L. Three-dimensional structures of avidin and the avidin-biotin complex. *Proc. Natl. Acad. Sci. U.S.A.* 1993, *90* (11), 5076-5080. DOI: doi:10.1073/pnas.90.11.5076.

(10) Pedersen, C. J. Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* 1967, *89*(10), 2495-2496. DOI: 10.1021/ja00986a052.

(11) Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. *Science* 2002, *295* (5564), 2418-2421. DOI: doi:10.1126/science.1070821.

(12) Fabbrizzi, L.; Poggi, A. Sensors and switches from supramolecular chemistry. *Chem. Soc. Rev.* 1995, *24* (3), 197–202, 10.1039/CS9952400197. DOI: 10.1039/CS9952400197.

(13) Uhlenheuer, D. A.; Petkau, K.; Brunsveld, L. Combining supramolecular chemistry with biology. *Chem. Soc. Rev.* 2010, *39* (8), 2817–2826, 10.1039/B820283B. DOI: 10.1039/B820283B.

(14) Ma, X.; Zhao, Y. Biomedical Applications of Supramolecular Systems Based on Host-Guest Interactions. *Chem. Rev.* 2015, *115* (15), 7794-7839. DOI: 10.1021/cr500392w.

(15) Ju, H.; Zhu, C. N.; Wang, H.; Page, Z. A.; Wu, Z. L.; Sessler, J. L.; Huang, F. Paper without a Trail: Time-Dependent Encryption using Pillar[5]arene-Based Host-Guest Invisible Ink. *Adv. Mater.* 2022, *34* (6), 2108163. DOI: https://doi.org/10.1002/adma.202108163.

(16) Wenz, G. Cyclodextrins as Building Blocks for Supramolecular Structures and Functional Units. *Angewandte Chemie International Edition in English* 1994, *33* (8), 803–822. DOI: https://doi.org/10.1002/anie.199408031.

(17) Wenz, G. An Overview of Host-Guest Chemistry and its Application to Nonsteroidal Anti-Inflammatory Drugs. *Clinical Drug Investigation* 2000, *19*(2), 21-25. DOI: 10.2165/00044011-200019002-00003.

(18) Zheng, J.; Nicovich, P. R.; Dickson, R. M. Highly fluorescent noble-metal quantum dots. *Annu. Rev. Phys. Chem.* 2007, *58*, 409-431.

(19) Choi, S.; Dickson, R. M.; Yu, J. Developing luminescent silver nanodots for biological applications. *Chem. Soc. Rev.* 2012, *41* (5), 1867–1891.

(20) Frank, A. J.; Cathcart, N.; Maly, K. E.; Kitaev, V. Synthesis of Silver Nanoprisms with Variable Size and Investigation of Their Optical Properties: A First-Year Undergraduate Experiment Exploring Plasmonic Nanoparticles. *J. Chem. Educ.* 2010, *87* (10), 1098-1101. DOI: 10.1021/ed100166g (acccessed 2013/05/10).

(21) Yu, J. From Coinage Metal to Luminescent Nanodots: The Impact of Size on Silver's Optical Properties. *J. Chem. Educ.* 2014, *91* (5), 701-704. DOI: 10.1021/ed400416b (acccessed 2014/05/22).

(22) Henglein, A. Small-Particle Research - Physicochemical Properties of

Extremely Small Colloidal Metal and Semiconductor Particles. *Chem. Rev.* 1989, *89* (8), 1861–1873.

(23) Evanoff, D. D.; Chumanov, G. Synthesis and optical properties of silver nanoparticles and arrays. *ChemPhysChem* 2005, *6* (7), 1221-1231. DOI: 10.1002/cphc.200500113.

(24) Yu, J. H.; Choi, S.; Dickson, R. M. Shuttle-Based Fluorogenic Silver-Cluster Biolabels. *Angew. Chem.-Int. Edit.* 2009, *48* (2), 318-320. DOI: 10.1002/anie.200804137.

(25) Yu, J.; Patel, S. A.; Dickson, R. M. In vitro and intracellular production of peptide-encapsulated fluorescent silver nanoclusters. *Angew. Chem.-Int. Edit.* 2007, *46* (12), 2028-2030.

(26) Adhikari, B.; Banerjee, A. Facile Synthesis of Water-Soluble Fluorescent Silver Nanoclusters and Hg-II Sensing. *Chem. Mat.* 2010, *22*(15), 4364–4371. DOI: 10.1021/cm1001253.

(27) Choi, S.; Park, S.; Lee, K.; Yu, J. Oxidant-resistant imaging and ratiometric luminescence detection by selective oxidation of silver nanodots. *Chem. Commun.* 2013, *49* (93), 10908-10910, 10.1039/C3CC45601C. DOI: 10.1039/c3cc45601c.

(28) Richards, C. I.; Choi, S.; Hsiang, J. C.; Antoku, Y.; Vosch, T.; Bongiorno, A.;
Tzeng, Y. L.; Dickson, R. M. Oligonucleotide-stabilized Ag nanocluster
fluorophores. *J. Am. Chem. Soc.* 2008, *130* (15), 5038-5039. DOI:

10.1021/ja8005644.

(29) Zhao, Y. L.; Choi, S.; Yu, J. H. In Situ Generated Silver Nanodot Forster Resonance Energy Transfer Pair Reveals Nanocage Sizes. *J. Phys. Chem. Lett.*2020, *11* (16), 6867–6872. DOI: 10.1021/acs.jpclett.0c01950.

(30) Wei, P.; Yan, X.; Huang, F. Supramolecular polymers constructed by orthogonal self-assembly based on host-guest and metal-ligand interactions. *Chem. Soc. Rev.* 2015, *44* (3), 815-832, 10.1039/C4CS00327F. DOI: 10.1039/C4CS00327F.

(31) Mann, S. Molecular recognition in biomineralization. *Nature* 1988, *332*(6160), 119-124. DOI: 10.1038/332119a0.

(32) Sarker, M.; Izadifar, M.; Schreyer, D.; Chen, X. Influence of ionic crosslinkers (Ca2+/Ba2+/Zn2+) on the mechanical and biological properties of 3D Bioplotted Hydrogel Scaffolds. *J. Biomater. Sci. Polym. Ed.* 2018, *29* (10), 1126-1154. DOI: 10.1080/09205063.2018.1433420.

(33) Zou, R.; Wang, Q.; Wu, J.; Wu, J.; Schmuck, C.; Tian, H. Peptide self-assembly triggered by metal ions. *Chem. Soc. Rev.* 2015, *44* (15), 5200-5219, 10.1039/C5CS00234F. DOI: 10.1039/C5CS00234F.

(34) Gal, A.; Wirth, R.; Kopka, J.; Fratzl, P.; Faivre, D.; Scheffel, A. Macromolecular recognition directs calcium ions to coccolith mineralization sites. *Science* 2016, *353* (6299), 590–593. DOI: doi:10.1126/science.aaf7889.

(35) Li, J.; Han, C.; Wu, W.; Zhang, S.; Guo, J.; Zhou, H. Selective and cyclic

detection of Cr3+ using poly(methylacrylic acid) monolayer protected gold nanoparticles. *New J. Chem.* 2014, *38* (2), 717-722, 10.1039/C3NJ00756A. DOI: 10.1039/C3NJ00756A.

(36) Knöfel, N. D.; Rothfuss, H.; Tzvetkova, P.; Kulendran, B.; Barner-Kowollik,
C.; Roesky, P. W. Heterobimetallic Eu(iii)/Pt(ii) single-chain nanoparticles: a path
to enlighten catalytic reactions. *Chem. Sci.* 2020, *11* (38), 10331-10336,
10.1039/D0SC03579C. DOI: 10.1039/D0SC03579C.

(37) Hu, J.; Xu, T.; Cheng, Y. NMR insights into dendrimer-based host-guest systems. *Chem. Rev.* 2012, *112* (7), 3856-3891.

(38) Murdey, R.; Stuckless, J. T. Calorimetry of Polymer Metallization: Copper,
Calcium, and Chromium on PMDA-ODA Polyimide. *J. Am. Chem. Soc.* 2003, *125*(13), 3995-3998. DOI: 10.1021/ja028829w.

(39) Moirangthem, M.; Arts, R.; Merkx, M.; Schenning, A. P. H. J. An Optical Sensor Based on a Photonic Polymer Film to Detect Calcium in Serum. *Adv. Funct. Mater.* 2016, *26* (8), 1154-1160. DOI: https://doi.org/10.1002/adfm.201504534.

(40) Wallace, M.; Holroyd, J.; Kuraite, A.; Hussain, H. Does It Bind? A Method to Determine the Affinity of Calcium and Magnesium Ions for Polymers Using 1H NMR Spectroscopy. *Anal. Chem.* 2022, *94* (31), 10976-10983. DOI: 10.1021/acs.analchem.2c01166.

(41) Sinn, C. G.; Dimova, R.; Antonietti, M. Isothermal Titration Calorimetry of

the Polyelectrolyte/Water Interaction and Binding of Ca2+: Effects Determining the Quality of Polymeric Scale Inhibitors. *Macromolecules* 2004, *37* (9), 3444-3450. DOI: 10.1021/ma030550s.

(42) Liu, X.; Zhu, J. Metal Ion-Sensing Polymer in the Weak Binding Monomer Regime. *J. Phys. Chem. B* 2009, *113* (24), 8214–8217. DOI: 10.1021/jp902951g.

(43) Gouanvé, F.; Schuster, T.; Allard, E.; Méallet-Renault, R.; Larpent, C. Fluorescence Quenching upon Binding of Copper Ions in Dye-Doped and Ligand-Capped Polymer Nanoparticles: A Simple Way to Probe the Dye Accessibility in Nano-Sized Templates. *Adv. Funct. Mater.* 2007, *17* (15), 2746-2756. DOI: https://doi.org/10.1002/adfm.200601056.

(44) Xu, H. X.; Suslick, K. S. Water-Soluble Fluorescent Silver Nanoclusters. *Adv. Mater.* 2010, *22* (10), 1078-1082. DOI: 10.1002/adma.200904199.

(45) Huard, D. J. E.; Demissie, A.; Kim, D.; Lewis, D.; Dickson, R. M.; Petty, J. T.;
Lieberman, R. L. Atomic Structure of a Fluorescent Ag8 Cluster Templated by a
Multistranded DNA Scaffold. *J. Am. Chem. Soc.* 2019, *141* (29), 11465–11470. DOI:
10.1021/jacs.8b12203.

(46) Choi, S.; Zhao, Y.; Yu, J. Generation of luminescent silver nanodots in the presence of amino silane and sodium polyacrylate. *J. Photochem. Photobiol. A* 2019, *374*, 36-42. DOI: https://doi.org/10.1016/j.jphotochem.2019.01.018.

(47) Hong, S.; Zhao, Y.; Choi, S.; Lee, E.; Yu, J. Tuning the fast generation of luminescent silver nanodots on a surface. *Chem. Commun.* 2022, *58* (57), 7916-

7919, 10.1039/D2CC02678C. DOI: 10.1039/D2CC02678C.

(48) Zhao, Y.: Choi, S.; Hong, S.; Lee, E.; Yu, J. Panchromatic Fluorogenic Generation of Luminescent Silver Nanodots by Cluster Transfer. Adv. Mater. Interfaces 2022, 9 (29), 2201121. DOI: https://doi.org/10.1002/admi.202201121.
(49) Jeon, S. M.; Choi, S.; Lee, K.; Jung, H.-S.; Yu, J. Significantly improved stability of silver nanodots via nanoparticles encapsulation. J. Photochem. Photobiol. A 2018, 355, 479-486. DOI: https://doi.org/10.1016/j.jphotochem.2017.05.045.

(50) Yang, S.-A.; Choi, S.; Jeon, S. M.; Yu, J. Silica nanoparticle stability in biological media revisited. *Scientific Reports* 2018, 8 (1), 185. DOI: 10.1038/s41598-017-18502-8.

(51) Shafirovich, V. Y.; Courtney, S. H.; Ya, N.; Geacintov, N. E. Proton-Coupled Photoinduced Electron Transfer, Deuterium Isotope Effects, and Fluorescence Quenching in Noncovalent Benzo[a]pyrenetetraol-Nucleoside Complexes in Aqueous Solutions. *J. Am. Chem. Soc.* 1995, *117* (17), 4920-4929. DOI: 10.1021/ja00122a024.

(52) Marras, S. A. E.; Kramer, F. R.; Tyagi, S. Efficiencies of fluorescence resonance energy transfer and contact<sup>-</sup>mediated quenching in oligonucleotide probes. *Nucleic Acids Res.* 2002, *30* (21), e122-e122. DOI: 10.1093/nar/gnf121 (acccessed 5/29/2023).

(53) Xie, S.; Wong, A. Y. H.; Chen, S.; Tang, B. Z. Fluorogenic Detection and

Characterization of Proteins by Aggregation-Induced Emission Methods. *Chemistry - A European Journal* 2019, *25* (23), 5824-5847. DOI: https://doi.org/10.1002/chem.201805297.

(54) Choi, S.; Jeong, Y.; Yu, J. Temperature and Viscosity Dependence of Gold Nanodot Luminescence. *Eur. J. Inorg. Chem.* 2017, *2017* (40), 4696-4701. DOI: 10.1002/ejic.201700722.

(55) Nau, W. Modern Molecular Photochemistry of Organic Molecules. by N. J.
Turro, V. Ramamurthy, J. C. Scaiano. *ChemPhysChem* 2011, *12* (13), 2496-2497.
DOI: https://doi.org/10.1002/cphc.201000976.

(56) Ozaki, T.; Funato, M.; Kawakami, Y. Origin of temperature-induced luminescence peak shifts from semipolar \$(11\overline{2}2)\$ \${\mathrm{In}}\_{x}{\mathrm{Ga}}\_{1\ensuremath{-}x}\mathrm{N}\$ quantum wells. *Phys. Rev. B* 2017, *96* (12), 125305. DOI: 10.1103/PhysRevB.96.125305.

(57) Abbyad, P.; Childs, W.; Shi, X.; Boxer, S. G. Dynamic Stokes shift in green fluorescent protein variants. *Proc. Natl. Acad. Sci. U.S.A.* 2007, *104*(51), 20189-20194. DOI: doi:10.1073/pnas.0706185104.

(58) Hu, H.; Saniger, J.; Garcia-Alejandre, J.; Castaño, V. M. Fourier transform infrared spectroscopy studies of the reaction between polyacrylic acid and metal oxides. *Mater. Lett.* 1991, *12* (4), 281-285. DOI: https://doi.org/10.1016/0167-577X(91)90014-W.

53

(59) Kirwan, L. J.; Fawell, P. D.; van Bronswijk, W. In Situ FTIR-ATR Examination of Poly(acrylic acid) Adsorbed onto Hematite at Low pH. *Langmuir* 2003, *19*(14), 5802-5807. DOI: 10.1021/la027012d.

(60) Ellerbrock, R. H.; Gerke, H. H. FTIR spectral band shifts explained by OMcation interactions. *J. Plant. Nutr. Soil Sci.* 2021, *184* (3), 388-397. DOI: https://doi.org/10.1002/jpln.202100056.

(61) Broeren, M. A. C.; de Waal, B. F. M.; van Genderen, M. H. P.; Sanders, H. M.
H. F.; Fytas, G.; Meijer, E. W. Multicomponent Host-Guest Chemistry of Carboxylic Acid and Phosphonic Acid Based Guests with Dendritic Hosts: An NMR Study. *J. Am. Chem. Soc.* 2005, *127* (29), 10334-10343. DOI: 10.1021/ja052074m.

(62) OGAWA, Y.; TANOKURA, M. Calcium Binding to Calmodulin: Effects of Ionic
Strength, Mg 2+ , pH and Temperature 1. *J. Biochem.* 1984, *95* (1), 19–28. DOI:
10.1093/oxfordjournals.jbchem.a134584 (acccessed 11/3/2022).

(63) Tsuchiya, H.; Sinawang, G.; Asoh, T.-a.; Osaki, M.; Ikemoto, Y.; Higuchi, Y.; Yamaguchi, H.; Harada, A.; Uyama, H.; Takashima, Y. Supramolecular Biocomposite Hydrogels Formed by Cellulose and Host-Guest Polymers Assisted by Calcium Ion Complexes. *Biomacromolecules* 2020, *21* (9), 3936-3944. DOI: 10.1021/acs.biomac.0c01095.

(64) Gilbert, P. U. P. A.; Bergmann, K. D.; Boekelheide, N.; Tambutté, S.; Mass, T.; Marin, F.; Adkins, J. F.; Erez, J.; Gilbert, B.; Knutson, V.; et al. Biomineralization: Integrating mechanism and evolutionary history. *Science Advances* 2022, *8*(10), eabl9653. DOI: doi:10.1126/sciadv.abl9653.

(65) Burlingame, G. A.; Dietrich, A. M.; Whelton, A. J. Understanding the basics of tap water taste. *Journal-American Water Works Association* 2007, *99*(5), 100-111.

## VI. 국문 초록

게스트 상대에 대한 가장 적합한 결합을 보여주는 선형 고분자의 명확한 입증은 아직 알려지지 않았다. 폴리아크릴산(PAA, poly acrylic acid)으로 안정화된 발광하는 은 나노닷(이하 PAA-AgNDs으로 기재)은 PAA 사슬과 결합 양이온 사이의 호스트-게스트 상호 작용을 모니터링하기 위해 턴온 센서(turn-on sensor)로 적용되었다. PAA의 카르복실레이트와 2족 양이온의 결합은 PAA 사슬의 강직성을 증가시키고, PAA-AgNDs의 비방사선 붕괴를 지연시키며, 결과적으로 은 나노닷의 발광 효율을 향상시키고 스펙트럼의 청색 이동을 유도하였다. 더불어, 아크릴아마이드 젤(acrylamide gel)을 사용한 간단한 시각화 방법과 여러 유형의 물을 사용한 간단한 실험은 PAA-AgNDs이 고분자와 2족 양이온 사이의 호스트-게스트 상호 작용을 탐지하는 데 탁월한 프로브가 될 수 있음을 보여주었다.

주요어: 은 나노닷, 폴리아크릴산, 호스트-게스트 화학, 2족 양이온

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"I can do everything through him who gives me strength." (Philippians 4:13)

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