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Poly-L-lysine-induced Self-association and Luminescence of Dicyanoaurate(I)

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The assembling and self-association of anionic $[Au(CN)_2]^-$ spatially along cationic β-sheeted poly-L-lysine, P(Lys), through electrostatic interaction was demonstrated to form luminescent $[Au(CN)_2]^-$ aggregates, wherein negatively charged $[Au(CN)_2]^-$ was found to stabilize the β-sheet structure by suppressing repulsion between the positively charged side chains.

Luminescent properties of closed shell d^{10} gold(I) complexes have attracted much attention because a closed shell d^{10} configuration does not allow low-lying d–d excited states.[1] Gold(I) complexes are known to aggregate through $d^{10}\cdots d^{10}$ closed shell aurophilic bonding interaction,[1c,2] which plays an important role in determining aggregated structures and luminescence properties.[1a,1c,1d,3] The emission of $[Au(CN)_2]^-$ in aqueous media has been demonstrated to be tunable based on the aggregation of $[Au(CN)_2]^-$ through aurophilicity although high concentration ($\geq 10^{-2}$ M) is required to exhibit luminescence at ambient temperature.[4] On the other hand, the utilization of polyelectrolytes as scaffolds has been recognized to be a reliable strategy for assembling opposite-charged functional moieties.[5] Anionic polyelectrolytes have been demonstrated to induce the aggregation of positively charged platinum(II) complexes, leading to luminescence change resulting from the metal–metal and π–π interactions.[5d–5f] We have also demonstrated that redox-active ferrocenes bearing a long alkylene chain are aggregated along the backbone of anionic double helical DNA, presenting a redox-active (outer) and hydrophobic (inner) sphere around the double helical core.[6] Poly-L-lysine (P(Lys)) exists in a random coil conformation at neutral pH due to the repulsion between the positively charged side chains and an α-helical conformation at above pH 10.6 due to the reduced charge on the side chains at a pH above the pK_a (10.5). Above pH 10.6, increasing temperature induces the transformation of an α-helical conformation into a β-sheet structure, which is stabilized by hydrophobic interaction between the side chains.[7] P(Lys) bearing multiple positively charged side chains is envisioned to serve as a spatially aligned polymeric scaffold for the aggregation and self-association of negatively charged $[Au(CN)_2]^-$ through electrostatic interaction. Also, aggregation of negatively charged $[Au(CN)_2]^-$ might influence the secondary structure of P(Lys) resulting from the stabilization of positive charges. From these points of view, we embarked upon the assembling and self-association of anionic $[Au(CN)_2]^-$ spatially along cationic β-sheeted P(Lys) to form luminescent $[Au(CN)_2]^-$ aggregates (Figure 1).

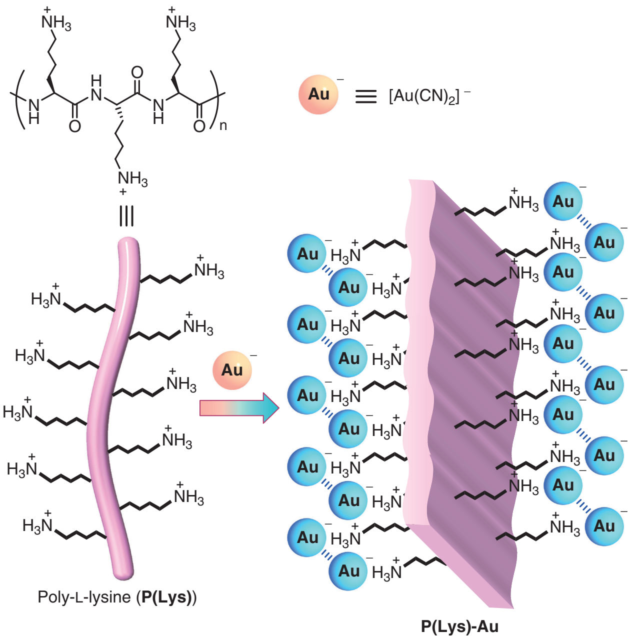

Figure 1. Schematic representation of P(Lys)-induced aggregation and self-association of $[Au(CN)_2]^-$.

P(Lys)-induced aggregation and self-association of $[Au(CN)_2]^-$ were investigated by UV–vis spectroscopy. Addition of P(Lys) (MW >8000 as obtained from PEPTIDE INSTITUTE, INC.) to a 1.0×10^{-3} M ultrapure water solution of $K[Au(CN)_2]$ exhibited the appearance of a new lower-energy absorption shoulder in the region of approximately 250–300 nm, and an increase in the ratio of the Lys unit to $K[Au(CN)_2]$ resulted in a gradual increase of the shoulder peak in the UV–vis spectra (Figure 2a). These observations indicate the oligomerization of $[Au(CN)_2]^-$ through electrostatic interaction with positively charged side chains and aurophilicity.

Circular dichroism (CD) spectrometry is a useful tool to determine an ordered structure in solution. The CD spectrum of P(Lys) in an ultrapure water solution at 298 K indicates a random coil conformation due to the electrostatic repulsion between the positively charged side chains (Figure 2b). With an increase in the ratio of $K[Au(CN)_2]$ to the Lys unit, an induced circular dichroism (ICD) at around 230 and 240 nm from the absorbance region of $[Au(CN)_2]^-$ appeared and became more negative as shown in Figure 2b, which indicates the assembling of anionic $[Au(CN)_2]^-$ spatially around the backbone of cationic P(Lys). Furthermore, an increase in the ratio of $K[Au(CN)_2]$ caused the intensity increase of a negative peak at around 212 nm although an ICD at around 230 and 240 nm was hardly changed. This result suggests the conformational change from the random coil to the β-sheet structure.[7] The aggregation of negatively charged $[Au(CN)_2]^-$ through the electrostatic interaction is thought to stabilize the β-sheet structure by suppressing repulsion between positively charged side chains. It is well known that biological activities of the proteins are closely related to the conformation,

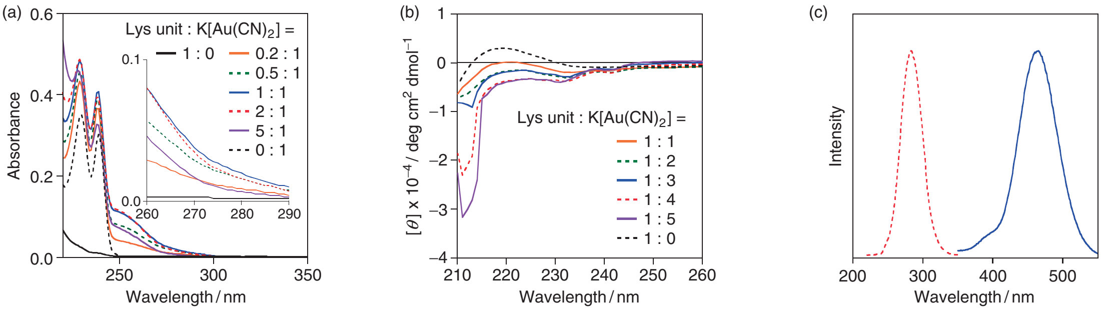

Figure 2. (a) UV–vis spectra of K[Au(CN)$_2$] (1.0 × 10^{-3} M) in an ultrapure water solution containing various amounts of P(Lys) (0, 0.2, 0.5, 1.0, 2.0, and 5.0 × 10^{-3} M Lys unit, respectively) at 298 K. (b) CD spectra of P(Lys) (1.0 × 10^{-3} M Lys unit) in an ultrapure water solution containing various amounts of K[Au(CN)$_2$] (0, 1.0, 2.0, 3.0, 4.0, and 5.0 × 10^{-3} M, respectively) at 298 K. (c) Excitation (left) and emission (right) spectra of K[Au(CN)$_2$] (5.0 × 10^{-3} M) with P(Lys) (Lys unit:K[Au(CN)$_2$] = 1:1) in an ultrapure water solution at 298 K.

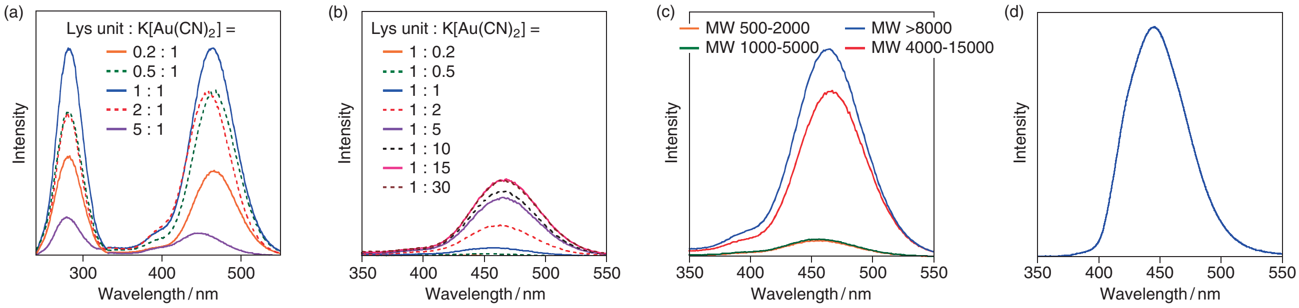

Figure 3. (a) Excitation (left) and emission (right) ($\lambda_{ex} = 280$ nm) of K[Au(CN)$_2$] (5.0 × 10^{-3} M) in an ultrapure water solution containing various amounts of P(Lys) (0, 1.0, 2.5, 5.0, 10.0, and 25.0 × 10^{-3} M Lys unit, respectively) at 298 K. (b) Emission spectra ($\lambda_{ex} = 280$ nm) of various amounts of K[Au(CN)$_2$] (1.0, 2.5, 5.0, 10.0, 25.0, 50.0, 75.0, and 150.0 × 10^{-4} M, respectively) in the presence of P(Lys) (5.0 × 10^{-4} M Lys unit) in an ultrapure water solution containing at 298 K. (c) Emission spectra ($\lambda_{ex} = 280$ nm) of K[Au(CN)$_2$] (5.0 × 10^{-3} M) in an ultrapure water solution containing equimolar concentration of the Lys unit of P(Lys) (MW 500–2000, MW 1000–5000, MW >8000, and MW 4000–15000, respectively) at 298 K. (d) Solid-state emission spectrum ($\lambda_{ex} = 340$ nm) of **P(Lys)–Au** at 298 K.

wherein secondary structures such as α-helices, β-sheets, and β-turns play an important role in protein folding. To the best of our knowledge, the stabilization of the β-sheet structure of P(Lys) by using negatively charged metal aggregates has not been reported although anionic surfactants have been demonstrated to induce the conformational change of P(Lys).[8]

P(Lys)-induced luminescence arising from aggregated [Au(CN)$_2$]$^-$ was observed by the addition of P(Lys) to a 5.0 × 10^{-3} M ultrapure water solution of K[Au(CN)$_2$]. The excitation and emission spectra of K[Au(CN)$_2$] with P(Lys) (Lys unit:K[Au(CN)$_2$] = 1:1) are shown in Figure 2c. Such luminescence was not detected in the absence of P(Lys). The influence of the ratio of the Lys unit to K[Au(CN)$_2$] on the self-association of anionic [Au(CN)$_2$]$^-$ was studied (Figure 3a). It is noteworthy that addition of 0.2 to 1 molar equivalents of the Lys unit of P(Lys) to K[Au(CN)$_2$] led to a gradual increase of the emission intensity and a slight blue shift of the emission band. Further addition of P(Lys) (1 to 5 molar equivalents of the Lys unit) caused a decrease in the emission intensity with a continuous blue shift of the emission band. The emission band of [Au(CN)$_2$]$^-$ is known to be red-shifted resulting from the oligomerization by increased concentration.[4] When P(Lys) loading per K[Au(CN)$_2$] is lowered, the ratio of [Au(CN)$_2$]$^-$ aggregates around the backbone of cationic P(Lys) is increased, which induces a red shift of the emission band. However, the emission intensity might be decreased because of the lowered ratio in complexation. High loading of P(Lys) per K[Au(CN)$_2$] would lead to the arrangement of [Au(CN)$_2$]$^-$ separately to the backbone of cationic P(Lys), which prevents the aggregation, causing the blue shift of the emission band and a decrease in the emission intensity. A gradual blue shift of the excitation band was observed by the continuous addition of P(Lys) (Figure 3a). The order of the emission intensity is consistent with the intensity of a new lower-energy absorption shoulder at around 280 nm (Figure 2a). These results support the P(Lys)-induced self-association and luminescence of [Au(CN)$_2$]$^-$.

A red shift of the emission band and a gradual increase in the emission intensity were observed as the amount of K[Au(CN)$_2$] increased as shown in Figure 3b, indicating the aggregation of anionic [Au(CN)$_2$]$^-$ around the backbone of cationic P(Lys). From the above-mentioned results, the aggregation and self-association of [Au(CN)$_2$]$^-$ are envisioned to be tunable by changing the polypeptide chain length. In fact, the luminescent properties of [Au(CN)$_2$]$^-$ distinctly depends on the polypeptide chain length in the emission spectra of K[Au(CN)$_2$] in the presence of P(Lys) with various chain lengths (Figure 3c). With P(Lys) (MW 500–2000) or P(Lys) (MW 1000–5000), a weak emission was observed probably due to the low aggrega-

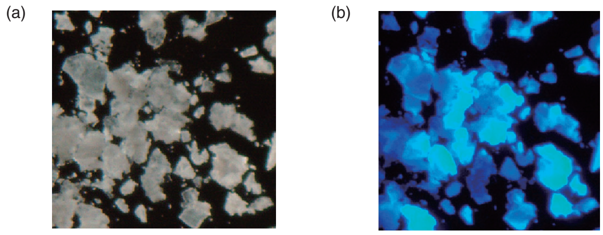

Figure 4. Photographs of **P(Lys)–Au** (a) under ambient light, (b) under UV irradiation with black light (365 nm).

tion ratio. On the contrary, higher molecular weight P(Lys) (MW >8000) or P(Lys) (MW 4000–15000) exhibited a promising luminescence from aggregated $[Au(CN)_2]^-$. These results support the above-mentioned results, its means, the P(Lys)-induced self-association and luminescence of $[Au(CN)_2]^-$.

Addition of 5 molar equivalents of a 0.5 M ultrapure water solution of $K[Au(CN)_2]$ to a 0.1 M Lys unit ultrapure water solution of P(Lys) afforded **P(Lys)–Au** as a white precipitate (Figures 1 and 4a).[9] **P(Lys)–Au** exhibited an intense blue emission with a maximum at 446 nm in a solid state at 298 K as depicted in Figure 3d. Under common UV light, $\lambda = 365$ nm, a distinct blue luminescence was observed (Figure 4b). The quantum yield of **P(Lys)–Au** at room temperature, measured in an integrating sphere for packed powder samples, is 0.36 using $\lambda_{ex} = 340$ nm.

In conclusion, poly-L-lysine, P(Lys), bearing multiple positively charged side chains was performed to serve as a spatially aligned polymeric scaffold for the aggregation and self-association of negatively charged $[Au(CN)_2]^-$ through electrostatic and aurophilic bonding interactions, wherein the tunable luminescence properties of $[Au(CN)_2]^-$ aggregates were demonstrated. The aggregation of negatively charged $[Au(CN)_2]^-$ spatially around the backbone of cationic P(Lys) was found to stabilize the β-sheet structure by suppressing repulsive forces between the positively charged side chains. Studies on the application of polypeptide-induced metal ion aggregates including functional materials and catalysts are now in progress.

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