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Polypeptides-Induced Self-Aggregation and Tuning of Emission Properties of Luminescent Complexes

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Summary: The assembling of anionic $[Au(CN)_2]^-$ spatially along cationic β-sheeted poly-L-lysine (**P(Lys)**) through electrostatic and aurophilic bonding interactions was demonstrated to form the luminescent $[Au(CN)_2]^-$ aggregate, wherein negatively charged $[Au(CN)_2]^-$ was found to stabilize the β-sheet structure by suppressing repulsion between the positively charged side chains. Poly-L-glutamic acid (**P(Glu)**) bearing multiple negatively charged side chains was performed to serve as a polymeric spatially aligned scaffold for aggregation of the positively charged platinum(II) complexes $[Pt(trpy)C{\equiv}CR](OTf)$ (trpy = 2,2′,6′,2″-terpyridine; R = Ph (**PtH**), $C_6H_4C_{12}H_{25}$-*p* (**PtC$_{12}$**)) through electrostatic interaction, resulting in tunable emission properties. The introduction of the cationic luminescent iridium(III) and ruthenium(II) complexes into **P(Glu)** as a polymeric scaffold, wherein control of the conformational change of **P(Glu)** was achieved, was also allowed to induce the tuning of the emission properties and energy transfer in aqueous media.

Keywords: aggregation; emission; gold(I) complex; iridium(III) complex; metallophilic interaction; platinum(II) complex; poly-L-glutamic acid; poly-L-lysine; ruthenium(II) complex; self-association

Introduction

Highly-ordered molecular assemblies are constructed in bio-systems to fulfill unique functions as observed in enzymes, receptors, etc. Architectural control of molecular aggregation is of importance for the development of functional materials.[1] Introduction of functional complexes into highly-ordered biomolecules is considered to be a convenient approach to novel biomaterials, bio-inspired systems, etc. The utilization of polyelectrolytes has been recognized to be a reliable strategy for the assembly of opposite-charged functional groups along the polyelectrolytes through electrostatic interaction.[2] In a previous paper, redox-active ferrocenes bearing a long alkylene chain were aggregated along the backbone of anionic double helical DNA, presenting redox-active (outer) and hydrophobic (inner) spheres around the double helical core.[3] Luminescent properties of d^{10} and d^8 transition metal complexes have attracted much attention because of their interesting luminescence properties based on metallophilic interaction.[4–5] Closed shell d^{10} gold(I) complexes are known to aggregate through $d^{10}\bullet\bullet\bullet d^{10}$ closed shell aurophilic bonding interaction,[4c,6] which plays an important role in determining aggregated structures and luminescence properties.[4a,4c,4d,7] Square-planar d^8 platinum(II) complexes with oligopyridine and cyclometalating ligands were demonstrated to show their interesting luminescence properties based on metallophilic interaction through $d_Z^2\bullet\bullet\bullet d_Z^2$ and/or π-π interactions.[5] Anionic polyelectrolytes were demonstrated to induce the aggregation of positively charged platinum(II) com-

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plexes, leading to luminescence change resulting from metal-metal and π-π interactions.[5m,5o,5r] Poly-L-lysine (**P(Lys)**) exists in a random coil conformation at neutral pH due to repulsion between 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. Poly-L-glutamic acid (**P(Glu)**) is also known to exist in an α-helix form at around pH 4.3 and a random coil conformation at a neutral pH due to repulsion between negatively charged side chains. In this paper, we summarize our ongoing research on controlled emission properties of luminescent complexes by using polypeptides as a polymeric spatially aligned scaffold.[8]

Tuning of Emission Properties of $[Au(CN)_2]^-$ Aggregate around P(Lys)

The emission of $[Au(CN)_2]^-$ in aqueous media was 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.[9] The aggregation and self-association of anionic $[Au(CN)_2]^-$ spatially along cationic β-sheeted **P(Lys)** was embarked upon to form the luminescent $[Au(CN)_2]^-$ aggregate (Figure 1). **P(Lys)**-induced aggregation and self-association of $[Au(CN)_2]^-$ were investigated in an ultra-pure water solution. Circular dichroism (CD) spectrometry is a useful tool to determine an ordered structure in solution. The CD spectrum of **P(Lys)** (MW >8000 as obtained from PEPTIDE INSTITUTE, INC.) in an ultra-pure water solution indicates a random coil conformation due to electrostatic repulsion between the positively charged side chains (Figure 2a). With 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, which indicates the assembling of anionic $[Au(CN)_2]^-$ spatially around the backbone of cationic **P(Lys)**. Furthermore, the increase in the ratio of $K[Au(CN)_2]$ caused the higher intensity of a negative peak at around 212 nm, suggesting the conformational change from the random coil to a β-sheet structure.[10] The aggregation of negatively charged $[Au(CN)_2]^-$ through electrostatic interaction is thought to stabilize the β-sheet structure of **P(Lys)** by suppressing repulsion between positively charged side chains. 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 demon-

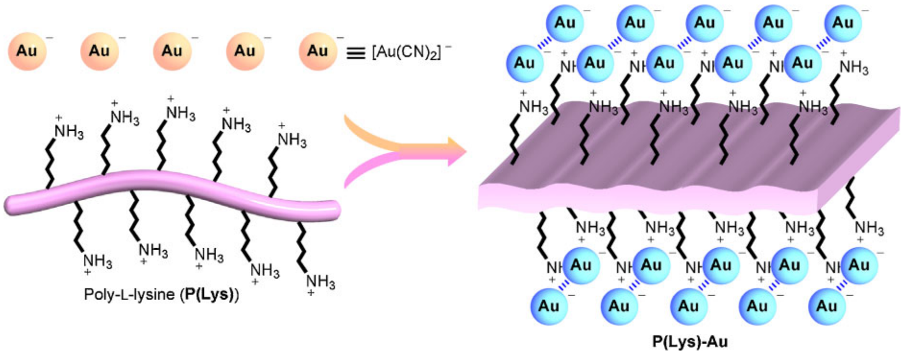

Figure 1.
Schematic representation of **P(Lys)**-induced aggregation and self-association of $[Au(CN)_2]^-$.

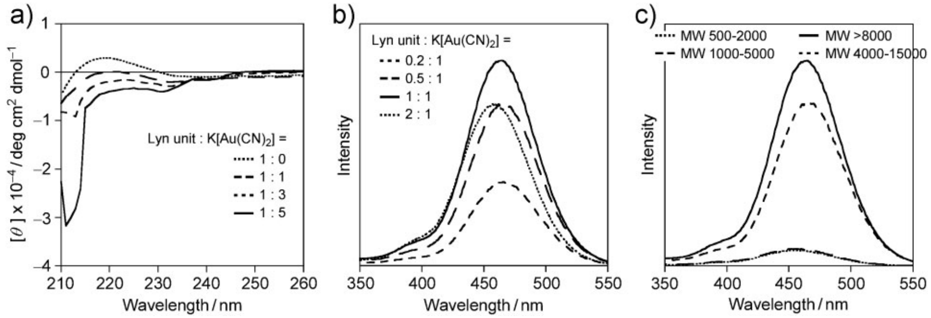

Figure 2.

(a) CD spectra of **P(Lys)** (1.0×10^{-3} M Lys unit) in an ultra-pure water solution containing various amounts of K[Au(CN)$_2$] (0, 1.0, 3.0, and 5.0×10^{-3} M, respectively) at 298 K. (b) Emission spectra ($\lambda_{ex} = 280$ nm) of K[Au(CN)$_2$] (5.0×10^{-3} M) in an ultra-pure water solution containing various amounts of **P(Lys)** (1.0, 2.5, 5.0, and 10.0×10^{-3} M Lys unit, respectively) at 298 K. (c) Emission spectra ($\lambda_{ex} = 280$ nm) of K[Au(CN)$_2$] (5.0×10^{-3} M) in an ultra-pure 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.

strated to induce the conformational change of **P(Lys)**.[11]

P(Lys)-induced luminescence arising from the aggregation of [Au(CN)$_2$]$^-$ was observed by the addition of **P(Lys)** to an ultra-pure water 5.0×10^{-3} M solution of K[Au(CN)$_2$] (Figure 2b). Such luminescence was not detected in the absence of **P(Lys)**. 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 slightly blue shift of the emission band. The emission band of [Au(CN)$_2$]$^-$ is known to be red-shifted through oligomerization by increased concentration.[9] 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.

Further addition of **P(Lys)** (1 to 2 molar equivalents of the Lys unit) caused a decrease in the emission intensity with a continuous blue shift of the emission band. 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 decrease in the emission intensity. These results support the **P(Lys)**-induced self-association and luminescence of [Au(CN)$_2$]$^-$.

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 depend 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 2c). With **P(Lys)** (MW 500–2000) or **P(Lys)** (MW 1000–5000), a weak emission was observed probably due to the low aggregation ratio. On the contrary, higher molecular weight **P(Lys)** (MW >8000) or **P(Lys)** (MW 4000–15000) exhibited a promising luminescence from [Au(CN)$_2$]$^-$ aggregates, supporting the above-mentioned results, its means, the **P(Lys)**-induced self-association and luminescence of [Au(CN)$_2$]$^-$.

Tuning of Emission Properties of Platinum(II) Aggregates Accommodated in P(Glu)

The aggregation of the cationic platinum(II) terpyridyl complexes with arylacetylide ligands [Pt(trpy)C≡CR](OTf) (trpy = 2,2′,6′,2″-terpyridine; R = Ph (**PtH**), $C_6H_4C_{12}H_{25}$-*p* (**PtC$_{12}$**)) spatially along the

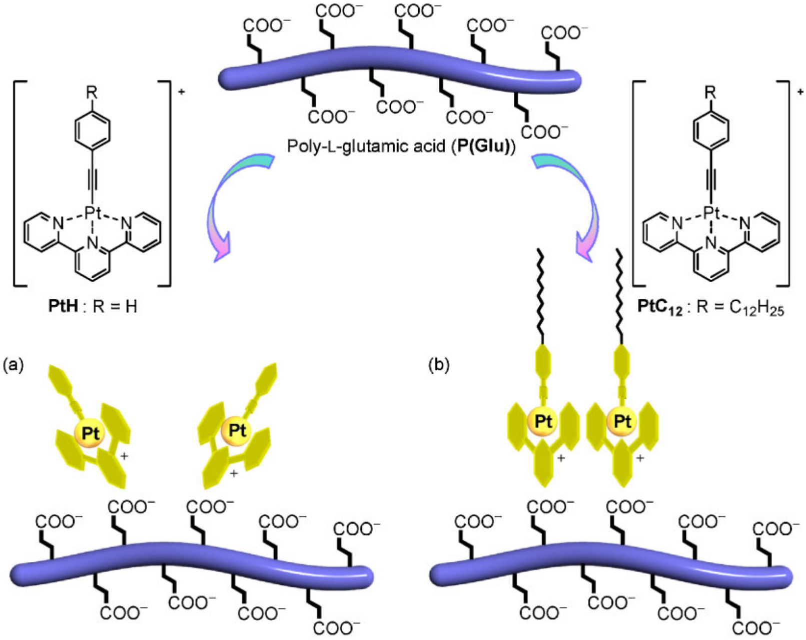

Figure 3.
Schematic representation of **P(Glu)**-induced aggregation for (a) **PtH** and (b) **PtC$_{12}$**.

anionic α-helical **P(Glu)** was investigated in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) solution to reveal the effect of the alkyl chain of the platinum(II) complexes in the formation of the platinum(II) aggregates accommodated in **P(Glu)** (Figure 3). An ICD at around 250–350 nm based on the absorbance region of the cationic platinum(II) complex **PtH** was observed with each mixture of **P(Glu)** and **PtH** (Figure 4a). These results suggest the aggregation of the cationic platinum(II) complex **PtH** spatially around the backbone of anionic **P(Glu)**. Also, negative double minima at 209 and 221 nm indicate the preservation of an α-helical structure of **P(Glu)**. The electrostatic interactions between the cationic platinum(II) complexes and negatively charged side chains of **P(Glu)** are thought to stabilize the α-helical structure by suppressing repulsion between negatively charged side chains.

PtH (5.0×10^{-5} M) showed weak emission based on the triplet metal-to-ligand charge transfer (^{3}MLCT)/the triplet ligand-to-ligand charge transfer (^{3}LLCT) at around 600 nm in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) solution probably due to solvent-induced quenching (Figure 4b). It is noteworthy mentioned that the addition of **P(Glu)** to the 5.0×10^{-5} M solution of **PtH** increased the emission intensity. Raise in the ratio of the Glu unit to **PtH** led to gradual increase of the emission intensity as shown in Figure 4b. **PtH** is considered to be accommodated in a hydrophobic sphere of **P(Glu)** to avoid the solvent effect. Furthermore, a new emission shoulder band was detected with an emission maximum at around 820 nm. The cationic platinum(II) terpyridyl complexes with arylacetylide ligands [Pt(trpy)C≡CR]$^+$ were reported to show the triplet metal-metal-to-ligand charge transfer (^{3}MMLCT) emission band at around 800 nm resulting from Pt(II)-Pt(II) and π-π interactions based on the aggregation.[5m,5q,5r,5s,5u] The new emission band at around 820 nm might be derived from the ^{3}MMLCT excited state resulting from Pt(II)-Pt(II) and π-π interactions based on the aggregation of **PtH**. **P(Glu)**

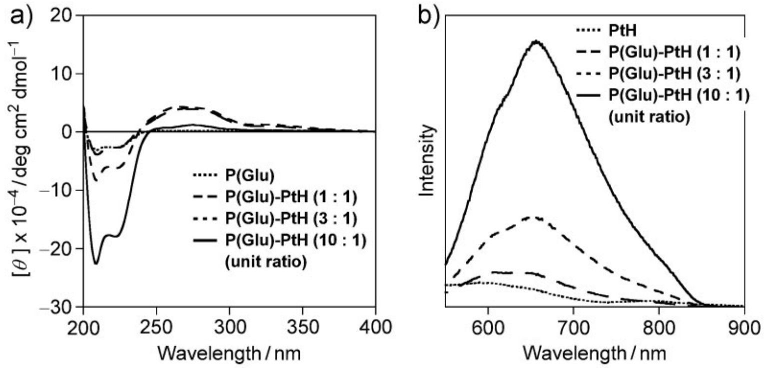

Figure 4.

(a) CD spectra of **P(Glu)** (5.0×10^{-5} M) and **PtH** (5.0×10^{-5} M) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) containing various amounts of **P(Glu)** (0.5, 1.5, and 5.0×10^{-4} M Glu unit, respectively) at 298 K. (b) Emission spectra ($\lambda_{ex} = 350$ nm) of **PtH** (5.0×10^{-5} M) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) containing various amounts of **P(Glu)** (0.0, 0.5, 1.5, and 5.0×10^{-4} M Glu unit, respectively) at 298 K.

bearing multiple negatively-charged side chains was found to serve as a polymeric spatially aligned scaffold for the accommodation and aggregation of cationic **PtH** (Figure 3a).

The accommodation of the cationic platinum(II) complex **PtC$_{12}$** having the dodecyl chain in a hydrophobic sphere of **P(Glu)** was also supported by the appearance of an ICD at around 250–350 nm based on the absorbance region of **PtC$_{12}$** in the CD spectra of **PtC$_{12}$** complex with **P(Glu)** as shown in Figure 5a. In comparison to the emission of **PtH**, the platinum(II) complex **PtC$_{12}$** (5.0×10^{-5} M) exhibited a strong emission based on ^{3}MLCT/^{3}LLCT at around 650 nm even in the absence of the **P(Glu)** as shown in Figure 5b. The complex **PtC$_{12}$** could assemble with ease in a polar environment. This result suggests the self-aggregation through hydrophobic interaction between the dodecyl chains to avoid the solvent effect. Interestingly, the ^{3}MMLCT emission at around 820 nm resulting from Pt(II)-Pt(II) and π-π interactions based on the aggregation of **PtC$_{12}$** was observed with

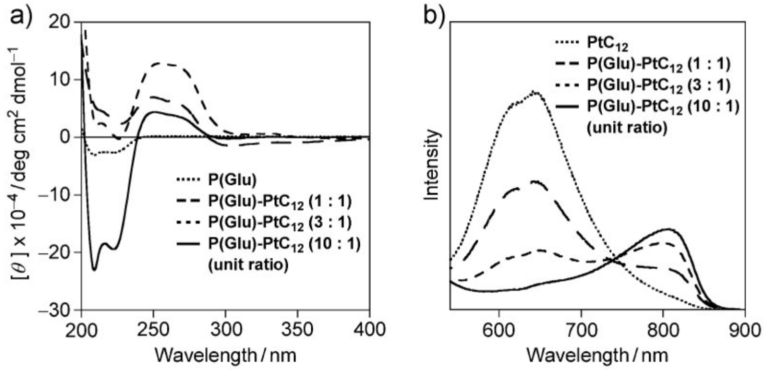

Figure 5.

(a) CD spectra of **P(Glu)** (5.0×10^{-5} M) and **PtC$_{12}$** (5.0×10^{-5} M) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) containing various amounts of **P(Glu)** (0.5, 1.5, and 5.0×10^{-4} M Glu unit, respectively) at 298 K. (b) Emission spectra ($\lambda_{ex} = 350$ nm) of **PtC$_{12}$** (5.0×10^{-5} M) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) containing various amounts of **P(Glu)** (0.0, 0.5, 1.5, and 5.0×10^{-4} M Glu unit, respectively) at 298 K.

concomitant disappearance of the ^{3}MLCT/^{3}LLCT emission by the addition of 100 mol% amount of **P(Glu)** to a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) solution of **PtC$_{12}$** (Figure 5b). This result indicates hydrophobic interaction between the dodecyl chains and electrostatic interaction between the cationic platinum(II) complexes and negatively charged side chains of **P(Glu)** to arrange the platinum(II) terpyridyl moieties regularly around the backbone of **P(Glu)** (Figure 3b). The dodecyl moiety of the platinum(II) complex was found to play an important role in the aggregation of the platinum(II) terpyridyl moieties to induce Pt(II)-Pt(II) and π-π interactions. Furthermore, raise in the ratio of **P(Glu)** caused gradual increase of the ^{3}MMLCT emission intensity with concomitant decrease of the ^{3}MLCT/^{3}LLCT emission intensity. High loading of **P(Glu)** per **PtC$_{12}$** would lead to the accommodation and aggregation of cationic **PtC$_{12}$** in a hydrophobic sphere of **P(Glu)**.

Tuning of Emission Properties of Cationic Luminescent Iridium(III) Complex Accommodated in P(Glu)

Luminescent iridium(III) complexes with cyclometalated ligands such as 2-phenylpyridine have been receiving much attention due to their promising electroluminescence applications.[12] The emission properties of these complexes have been demonstrated to be dependent on the cyclometalating ligand and polarity of solvents. The introduction of the cationic cyclometalated iridium(III) complex [Ir(ppyFF)$_2$(bpy)]Cl (**Ir(F)**) (where ppyFF = 2-(2,4-difluorophenyl)pyridine) into anionic α-helical **P(Glu)** was investigated (Figure 6). The CD spectrum of **P(Glu)** in a water solution at 298 K indicates a random coil conformation due to electrostatic repulsion between the negatively charged side chains (Figure 7a). The CD spectra of **Ir(F)** with **P(Glu)** showed an ICD at around 230–330 nm based on the absorbance region of **Ir(F)**. This result suggests the accomodation of the cationic complex **Ir(F)** spatially around the backbone of anionic **P(Glu)**. Furthermore, negative double minima at 210 and 221 nm in the CD spectrum of the 1:1 ratio indicate the formation of an α-helical structure. The aggregation of positively charged **Ir(F)** through the electrostatic interaction is thought to stabilize the α-helical structure by suppressing repulsion between negatively charged side chains. Further addition of **P(Glu)** to **Ir(F)** caused a conformational change from the α-helical structure to a random coil. The controlled conformational change (random coil – α-helical structure – random coil) of **P(Glu)** was performed by changing the raitio of **Ir(F)** and **P(Glu)**. The accommodation of the cationic complex **Ir(F)** in a hydrophobic sphere of **P(Glu)** led to the enhancement of the emission intensity. It is noteworthy that increasing the ratio of the Glu unit of **P(Glu)** to **Ir(F)** led to a gradual increase of the emission intensity and a slightly blue shift of the emission band (Figure 7b). The quantum yield of a water solution of **Ir(F)** with **P(Glu)** (10 molar equivalents of the Glu unit) is 28%.

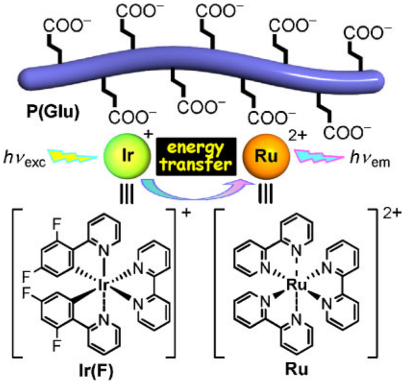

Figure 6.
Schematic representation of the introduction of the cationic iridium(III) complex **Ir(F)** with/without ruthenium(II) complex **Ru** into **P(Glu)** bearing multiple negatively charged side chains.

We embarked upon the introduction of the iridium(III) complex **Ir(F)** as an energy donor and the ruthenium(II) complex [Ru(bpy)$_3$]Cl$_2$ (**Ru**) as an energy acceptor into **P(Glu)** bearing multiple negatively charged side chains is envisioned to induce

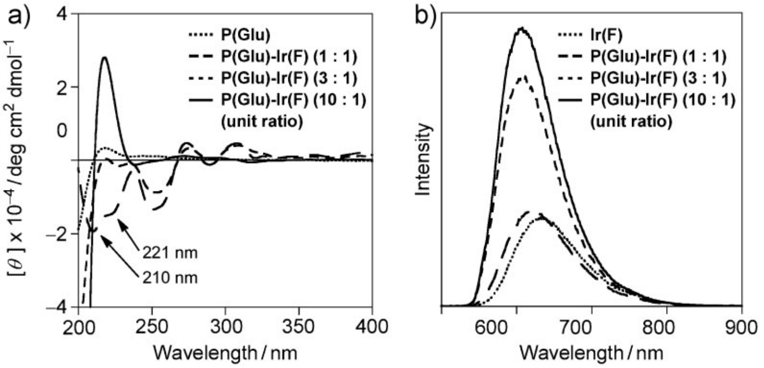

Figure 7.

(a) CD spectra of **P(Glu)** and [Ir(ppyFF)$_2$(bpy)]Cl (**Ir(F)**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0.5, 1.5, and 5.0×10^{-4} M Glu unit, respectively) at 298 K. (b) Emission spectra ($\lambda_{ex} = 310$ nm) of [Ir(ppyFF)$_2$(bpy)]Cl (**Ir(F)**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0, 0.5, 1.5, and 5.0×10^{-4} M Glu unit, respectively) at 298 K.

an efficient energy transfer (ET) based on spatial proximity between accommodated donor and acceptor complexes in a hydrophobic sphere of **P(Glu)**. The emission spectrum of a 10:1:1 mixture of **P(Glu)**, **Ir(F)**, and **Ru** upon excitation at 290 nm is shown in Figure 8a. By the addition of **P(Glu)**, the decrease of the characteristic emission at around at 500 nm from the excited state of **Ir(F)** was observed with concomitant increase of the emission intensity of **Ru** at around 625 nm. The excitation spectrum of **Ru** emission ($\lambda_{em} = 800$ nm) corresponds to the absorption profile of **Ir(F)**. From these results, an efficient ET process from the excited state of **Ir(F)** to **Ru** might occur in a hydrophobic sphere of **P(Glu)**. Such quenching of **Ir(F)** based on ET was not observed in a 10:1:1 mixture of NaCl, **Ir(F)**, and **Ru** (Figure 8b), indicating that **P(Glu)** plays an important role as a polymeric spatially aligned scaffold to accommodate the cationic complexes **Ir(F)** and **Ru** in a hydrophobic sphere of **P(Glu)**.

Conclusion

Polypeptide-induced tunable emission properties of gold(I), platinum(II), and

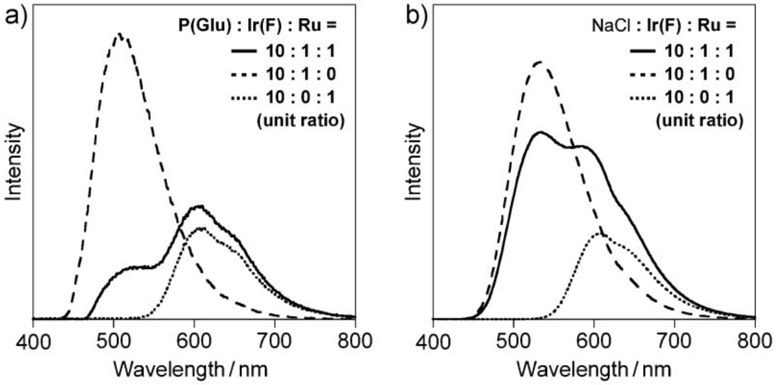

Figure 8.

(a) Emission spectra ($\lambda_{ex} = 290$ nm) of a mixture of **P(Glu)**, **Ir(F)**, and **Ru** (2.0×10^{-5} M **Ir(F)** and **Ru** unit) in a water solution at 298 K. (b) Emission spectra ($\lambda_{ex} = 290$ nm) of a mixture of NaCl, **Ir(F)**, and **Ru** (2.0×10^{-5} M **Ir(F)** and **Ru** unit) in a water solution at 298 K.

iridium(III) complexes were demonstrated. Poly-L-lysine, **P(Lys)**, bearing multiple positively charged side chains was performed to serve as a polymeric spatially aligned scaffold for the aggregation and self-association of negatively charged $[Au(CN)_2]^-$ through electrostatic and aurophilic bonding interactions. 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. Poly-L-glutamic acid, **P(Glu)**, bearing multiple negatively charged side chains was demonstrated to serve as a polymeric spatially aligned scaffold for the aggregation of the positively charged platinum(II) terpyridyl complexes with arylacetylide ligands through the electrostatic and hydrophobic interactions. The dodecyl moiety of the platinum(II) complex was found to play an important role in the aggregation of the platinum(II) terpyridyl moieties to induce the Pt(II)-Pt(II) and π-π interactions. Tuning of the emission properties of the cationic luminescent iridium(III) complexes in aqueous media was also performed by the introduction into **P(Glu)**. The introduction of the iridium(III) complex as an energy donor and the ruthenium(II) complex as an energy acceptor into **P(Glu)** was demonstrated to induce an efficient ET based on spatial proximity in a hydrophobic sphere of **P(Glu)**.

The architectural control of molecular assemblies utilizing biomolecules is envisioned to be a useful approach to artificial highly-ordered bioorganometallic systems, which is hybrids of biomolecules and organometallics. Studies on the application of polypeptide-induced metal ion aggregates including functional materials and catalysts are now in progress.

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