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Poly(L-glutamic acid)-modulated Emission Properties of Iridium(III) Complexes in an Aqueous Media

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The introduction of the cationic luminescent iridium(III) and ruthenium(II) complexes into negatively charged poly(L-glutamic acid) (**P(Glu)**) as a polymeric scaffold, wherein control of the conformational change of **P(Glu)** was achieved, was allowed to induce the tuning of the emission properties and energy transfer in an aqueous media.

Luminescent iridium(III) complexes with cyclometalated ligands such as 2-phenylpyridine have been receiving much attention due to their promising electroluminescence applications.[1] The emission properties of these complexes have been demonstrated to be dependent on the cyclometalating ligand and polarity of solvents. On the other hand, biomolecules are known to exist in a highly ordered structure to fulfill specific functions as observed in the double helix of DNA or α-helix and β-sheet of peptides. The introduction of functional complexes into such highly ordered biomolecules is envisioned to provide new bioconjugate materials. The utilization of double helical DNA or polypeptides as polyelectrolytes has been recognized to be a reliable strategy for assembling opposite-charged functional groups.[2] We have 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.[3] Poly(L-glutamic acid) (**P(Glu)**) is 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. **P(Glu)** bearing multiple negatively charged side chains has been demonstrated to induce the aggregation of positively charged luminescent platinum(II) complexes, leading to luminescence change resulting from the metal–metal and π–π interactions.[2f,2g,2i,2l,2m] From these points of view, we herein report the introduction of cationic cyclometalated iridium(III) and tris(2,2′-bipyridyl)ruthenium(II) complexes into negatively charged **P(Glu)** as a polymeric spatially aligned scaffold in an aqueous media, allowing a tuning of the emission properties (Figure 1).

The introduction of the cationic cyclometalated iridium(III) complex [Ir(ppy)$_2$(bpy)]Cl (**Ir**) (where ppy: 2-phenylpyridine, bpy: 2,2′-bipyridine) into anionic α-helical **P(Glu)** was investigated by UV–vis spectroscopy (Figure 2a). The addition of 100 mol % (based on the Glu unit) of poly(L-glutamic acid sodium salt) to a water solution of **Ir** led to the increase of the metal-to-ligand charge-transfer (MLCT) transition at around 300 nm, and the increased ratio of the Glu unit to **Ir** resulted in gradual increase of the peak in the UV–vis spectra (5.0×10^{-5} M **Ir** unit) as shown in Figure 2a. Circular dichroism (CD) spectrometry is a useful tool to determine an ordered structure in solution. 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 2b). An induced circular dichroism (ICD) at around 230–330 nm based on the absorbance region of **Ir** was observed in the CD spectra of a mixture of **P(Glu)** and **Ir** (Figure 2b). These results suggest the accommodation of the cationic complex **Ir** 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** 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** caused a conformational change from the α-helical structure to a random coil.

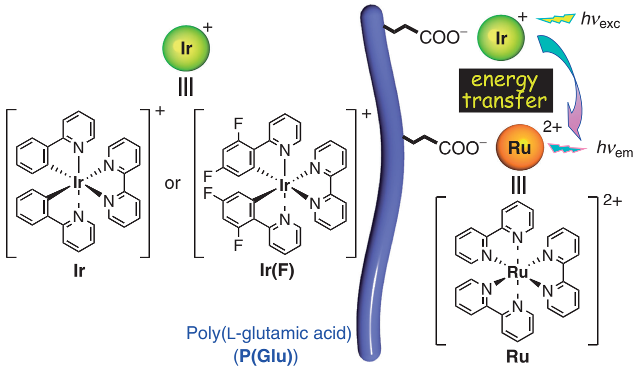

Figure 1. Schematic representation of the introduction of the cationic iridium(III) complex **Ir** or **Ir(F)** with/without ruthenium(II) complex **Ru** into **P(Glu)** bearing multiple negatively charged side chains.

The cationic cyclometalated iridium(III) complex **Ir** showed weak emission in a water solution (Figure 2c). The enhancement of the emission intensity was observed by the addition of **P(Glu)** to a water solution of **Ir**. The influence of the ratio of the Glu unit to **Ir** on the emission properties was studied. It is noteworthy that increasing the ratio of the Glu unit of **P(Glu)** to **Ir** led to a gradual increase of the emission intensity and a slight blue shift of the emission band (Figures 2c and 2d). The quantum yield of a water solution of **Ir** with **P(Glu)** (10 molar equivalents of the Glu unit) is 5%. The cyclometalated iridium(III) complexes are known to show an emission maximum with higher energy and stronger emission in the less polar solvent than in the more polar water.[4] As one possibility, the iridium(III) complex **Ir** is suggested to be accommodated in a hydrophobic sphere of **P(Glu)** to protect the excited state of the iridium complex against interaction with water. High loading of

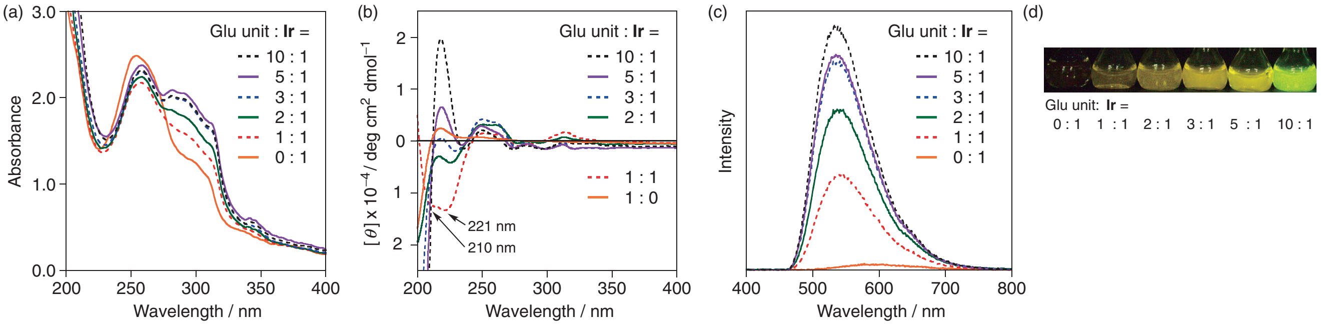

Figure 2. (a) UV–vis spectra of $[Ir(ppy)_2(bpy)]Cl$ (**Ir**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0, 0.5, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) at 298 K. (b) CD spectra of **P(Glu)** and $[Ir(ppy)_2(bpy)]Cl$ (**Ir**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0.5, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) at 298 K. (c) Emission spectra ($\lambda_{ex} = 310$ nm) of $[Ir(ppy)_2(bpy)]Cl$ (**Ir**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0, 0.5, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) at 298 K. (d) Photographs of the solution of $[Ir(ppy)_2(bpy)]Cl$ (**Ir**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0, 0.5, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) under UV irradiation with black light (365 nm).

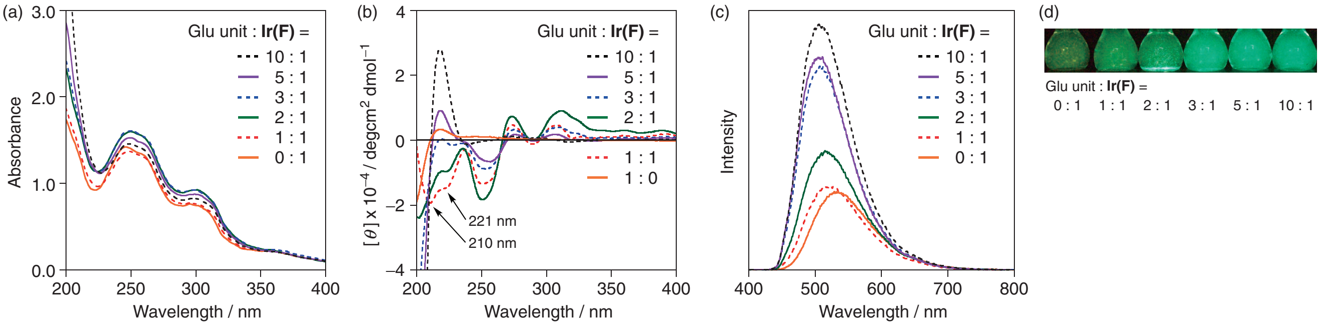

Figure 3. (a) UV–vis spectra of $[Ir(ppyFF)_2(bpy)]Cl$ (**Ir(F)**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0, 0.5, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) at 298 K. (b) CD spectra of **P(Glu)** and $[Ir(ppyFF)_2(bpy)]Cl$ (**Ir(F)**) (5.0×10^{-5} M) in a water solution containing various amounts of **P(Glu)** (0.5, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) at 298 K. (c) 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, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) at 298 K. (d) Photographs of the solution 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, 1.0, 1.5, 2.5, and 5.0×10^{-4} M Glu unit) under UV irradiation with black light (365 nm).

P(Glu) per **Ir** would lead to the accommodation in the sphere of **P(Glu)**, resulting in the enhancement of the emission intensity. **P(Glu)** bearing multiple negatively charged side chains was found to serve as a reliable polymeric scaffold for the accommodation of **Ir**.

The cationic cyclometalated iridium(III) complex $[Ir(ppyFF)_2(bpy)]Cl$ (**Ir(F)**) (where ppyFF: 2-(2,4-difluorophenyl)pyridine)[5,6] could be introduced into **P(Glu)**. The gradual increase of the MLCT transition at around 300 nm was observed by increasing in the ratio of the Glu unit to **Ir(F)** in the UV–vis spectra of **Ir(F)** (5.0×10^{-5} M **Ir(F)** unit) as shown in Figure 3a. 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)** (Figure 3b), suggesting the accommodation of the cationic complex **Ir(F)** in the sphere of **P(Glu)**. The controlled conformational change (random coil–α-helical structure–random coil) of **P(Glu)** was also performed by changing the ratio of **Ir(F)** and **P(Glu)** (Figure 3b). The accommodation of the cationic complex **Ir(F)** in the sphere of **P(Glu)** led to the enhancement of the emission intensity and a slight blue shift of the emission band (Figures 3c and 3d), wherein the quantum yield of a water solution of **Ir(F)** with **P(Glu)** (10 molar equivalents of the Glu unit) is 28%.

The introduction of energy donor and acceptor complexes into **P(Glu)** bearing multiple negatively charged side chains is envisioned to induce an efficient energy transfer (ET) based on spatial proximity between accommodated donor and acceptor complexes in the sphere of **P(Glu)**. 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. 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 4a. By the addition of **P(Glu)**, the decrease of the characteristic emission at around 500 nm from the excited state of **Ir(F)** was observed with concomitant increase of the emission intensity of **Ru** at around 625 nm as shown in Figure 4a. The excitation spectrum of **Ru** emission ($\lambda_{em} = 800$ nm) corresponds to the absorption profile of **Ir(F)**.[6] From these results, an efficient ET process from the excited state of **Ir(F)** to **Ru** might occur in the 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 4b), suggesting that **P(Glu)** plays an important role as a

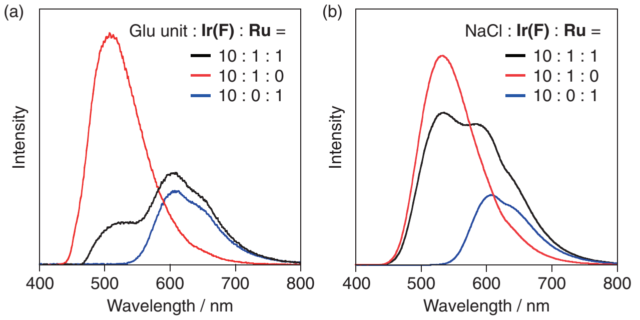

Figure 4. (a) Emission spectra ($\lambda_{ex} = 290$ nm) of a mixture of **P(Glu)**, [Ir(ppyFF)$_2$(bpy)]Cl (**Ir(F)**), and [Ru(bpy)$_3$]Cl$_2$ (**Ru**) (2.0×10^{-5} M **Ir(F)** and **Ru** unit) in a water solution at 298 K. (b) Emission spectra ($\lambda_{ex} = 290$ nm) of a mixture of NaCl, [Ir(ppyFF)$_2$(bpy)]Cl (**Ir(F)**), and [Ru(bpy)$_3$]Cl$_2$ (**Ru**) (2.0×10^{-5} M **Ir(F)** and **Ru** unit) in a water solution at 298 K.

polymeric spatially aligned scaffold to accommodate the cationic complexes **Ir(F)** and **Ru** in the sphere of **P(Glu)**.[2l,2m] **P(Glu)**-induced ET was also performed in the aggregated system of **Ir** and **Ru** in **P(Glu)**.[6]

In conclusion, the tuning of the emission properties of the cationic luminescent iridium(III) complexes in an aqueous media was demonstrated by the introduction into negatively charged poly(L-glutamic acid) (**P(Glu)**) as a polymeric spatially aligned scaffold. The introduction of the iridium(III) complex as an energy donor and the ruthenium(II) complex as an energy acceptor into **P(Glu)** was also performed to induce an efficient ET based on spatial proximity in the sphere of **P(Glu)**. The architectural control of molecular assemblies utilizing polypeptides as a polymeric spatially aligned scaffold, which possess chiral centers and the highly ordered structures, is envisioned to be a useful approach to artificial highly ordered systems without use of complicated chemical synthesis. Studies on the application of polypeptide-induced metal ion aggregates including functional materials and catalysts are now in progress.

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5 **Crystal data for Ir(F)**: $C_{32}H_{20}N_4F_4Cl_1Ir_1 \cdot 3CHCl_3$, $M_r = 1122.34$, monoclinic, space group $P2_1/a$ (No. 14), $a = 16.1522(4)$ Å, $b = 14.6388(4)$ Å, $c = 17.8595(5)$ Å, $\beta = 101.4523(8)°$, $V = 4138.8(2)$ Å^3, $Z = 4$, $T = -100$ °C, $D_{calcd} = 1.801$ g cm^{-3}, μ(Mo Kα) $= 39.300$ cm^{-1}, Mo Kα radiation ($\lambda = 0.71075$ Å), $R1 = 0.043$, $wR2 = 0.112$. CCDC-829169.

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.