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## Emission properties of platinum(II) terpyridyl complexes with hydrophobic poly-L-glutamic acid

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The reaction of sodium salt of poly-L-glutamic acid (P(Glu)) with didodecyldimethylammonium (DDA) bromide was demonstrated to afford **P(Glu)-DDA**, which was confirmed to form the  $\alpha$ -helical structure even in methanol. The introduction of 0.2 equiv. amount of the platinum(II) complex [Pt(trpy)C $\equiv$ CPhC<sub>12</sub>H<sub>25-p</sub>](OTf) (trpy = 2,2',6',2''-terpyridine; **PtC<sub>12</sub>**) into **P(Glu)-DDA** in methanol was found to induce the aggregation of platinum(II) complexes, resulting in the exhibition of the triplet metal-metal-to-ligand charge transfer emission. Such synergistic effect was not observed in the case of the platinum(II) complex [Pt(trpy)C $\equiv$ CPh](OTf) (**PtH**), wherein the emission intensity based on metal-to-ligand charge transfer/ligand-to-ligand charge transfer was increased.

**Keywords:** poly-L-glutamic acid; platinum(II) complex; emission properties

### 1. Introduction

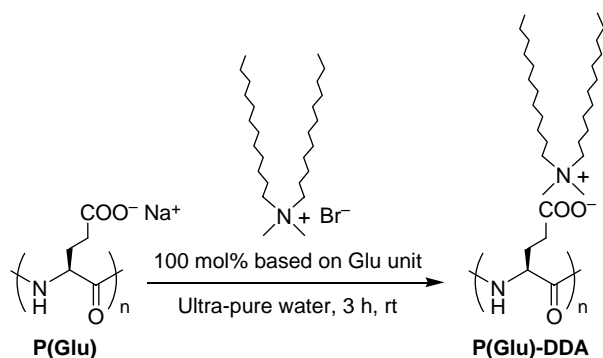
Recently, the research field of bioorganometallic chemistry, which is a hybrid area between biochemistry and organometallic chemistry, has drawn much attention (1–4). Conjugation of organometallic compounds with biomolecules such as DNA, amino acids and peptides is envisioned to provide novel systems depending on both properties. Square-planar d<sup>8</sup> transition metal complexes possess the intriguing photophysical and photochemical properties. In particular, luminescent platinum(II) complexes with oligopyridine or cyclometallating ligands have attracted much attention because of their interesting luminescence properties based on metallophilic interaction through d<sub>Z<sup>2</sup></sub>–d<sub>Z<sup>2</sup></sub> and/or  $\pi$ – $\pi$  interactions (5–25). Introduction of functional complexes into highly ordered biomolecules is considered to be a convenient approach to novel biomaterials, bio-inspired systems, etc. The non-covalent bond is a powerful tool in the construction of architectural molecular assemblies. The utilisation of polyelectrolytes as scaffolds has been recognised to be a reliable strategy for assembling opposite-charged functional moieties (16, 18, 21, 26–28). In a previous paper, the redox-active ferrocene bearing a long alkylene chain has been aggregated along the backbone of anionic double helical DNA, presenting a redox-active (outer) and hydrophobic (inner) sphere around the double helical core (29). We have also demonstrated that poly(allylamine hydrochloride) and poly-L-lysine hydrobromide bearing positively charged side chains along the polymer chain serve as a polymeric spatially aligned scaffold for aggregation and self-association of negatively charged [Au(CN)<sub>2</sub>]<sup>–</sup> through electrostatic interaction to afford the

luminescent [Au(CN)<sub>2</sub>]<sup>–</sup> aggregate (30, 31). Poly-L-glutamic acid (P(Glu)) exists in a random coil conformation at a neutral pH due to repulsion between negatively charged side chains, and an  $\alpha$ -helical conformation at around pH 4.3 due to the reduced charge on the side chains. The carboxylate moieties of the side chains are expected to assemble cationic metal complexes along the exterior of P(Glu). Anionic polyelectrolytes such as single-stranded nucleic acids, P(Glu) and poly(acrylic acid)-induced metal–metal interaction and concomitant luminescence have been reported with alkynylplatinum(II) complexes (16, 18, 21). The introduction of hydrophobic moieties into P(Glu) is envisioned to afford a hydrophobic sphere around P(Glu), which can assemble functional moieties through hydrophobic interaction. We herein report the stabilisation of an  $\alpha$ -helical structure of P(Glu) in methanol by the introduction of didodecyldimethylammonium (DDA) bromide as a cationic surfactant to form the hydrophobic P(Glu) and the controlled emission properties of platinum(II) terpyridyl complexes with arylacetylide ligands accommodated around the hydrophobic P(Glu).

### 2. Results and discussions

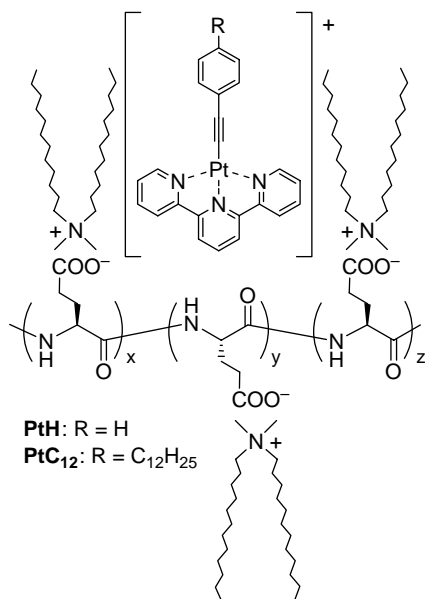
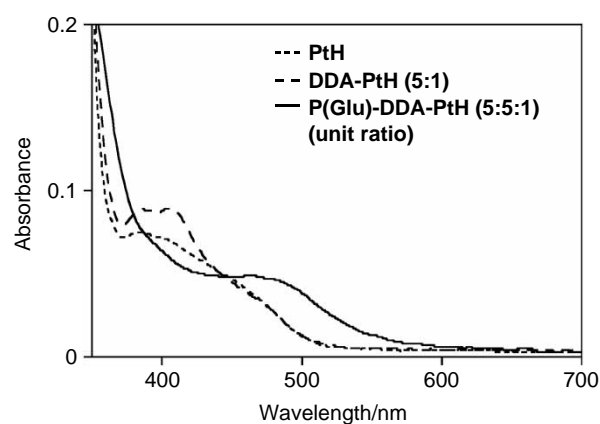
The reaction of sodium salt of P(Glu) (MW > 8000 obtained from the Peptide Institute, Inc., Ibaraki, Japan) with 100 mol% (based on the Glu unit) amount of DDA bromide in ultra-pure water at room temperature afforded **P(Glu)-DDA** as a white solid, which was soluble in methanol (Figure 1). Circular dichroism (CD) spectrometry is a useful tool to determine an ordered structure

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Figure 1. Synthesis of **P(Glu)-DDA**.

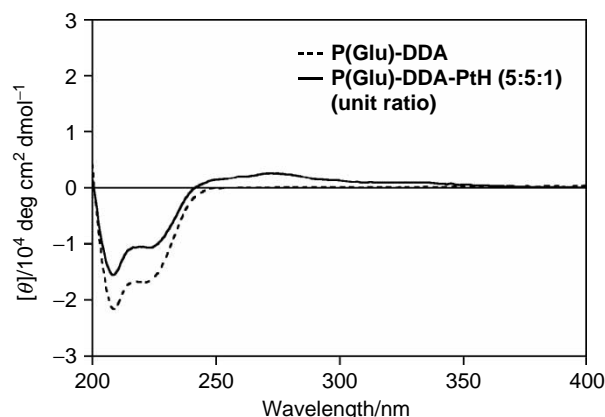
in the solution. **P(Glu)-DDA** in methanol exhibited a CD spectrum with strong negative double minima at 209 and 221 nm similar to the  $\alpha$ -helical **P(Glu)** in aqueous solution (Figure 4). From this result, the **P(Glu)-DDA** complex is suggested to form the ordered  $\alpha$ -helical structure even in methanol.

**P(Glu)-DDA** is envisioned to accommodate functional compounds in a hydrophobic sphere along the backbone of anionic helical **P(Glu)** through electrostatic and hydrophobic interactions. We embarked upon the introduction of cationic platinum(II) terpyridyl complexes with arylacetylide ligands [Pt(trpy)C $\equiv$ CR](OTf) (trpy = 2,2',6',2''-terpyridine; R = Ph (**PtH**), PhC<sub>12</sub>H<sub>25</sub>-*p* (**PtC<sub>12</sub>**), Figure 2) into **P(Glu)-DDA** to form the luminescent platinum(II) aggregates. **P(Glu)-DDA**-induced aggregation of the platinum(II) complexes was investigated by UV-vis spectroscopy. The addition of 500 mol% (based on the Glu unit) amount of **P(Glu)-DDA** to the methanol solution

Figure 2. Schematic representation of **P(Glu)-DDA-Pt(II)**.Figure 3. UV-vis spectra of **PtH**, **DDA-PtH** (5:1) and **P(Glu)-DDA-PtH** (5:5:1) in methanol (**PtH** unit:  $5.0 \times 10^{-5}$  M) at 298 K.

of the platinum(II) complex **PtH** ( $5.0 \times 10^{-5}$  M **PtH** unit) led to appearance of a new shoulder band at around 500 nm in the UV-vis spectra (Figure 3). An induced CD (ICD) at around 250–350 nm based on the absorbance region of **PtH** appeared in the CD spectrum of the complex of **P(Glu)-DDA** with **PtH** as shown in Figure 4. These results indicate the aggregation of **PtH** spatially around the backbone of anionic **P(Glu)**.

**PtH** ( $5.0 \times 10^{-5}$  M) showed a weak emission based on the triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT)/the triplet ligand-to-ligand charge transfer (<sup>3</sup>LLCT) at around 630 nm, in methanol probably due to the solvent-induced quenching (Figure 5). Interestingly, a strong emission at around 660 nm was observed by the addition of 500 mol% amount of **P(Glu)-DDA** to a methanol  $5.0 \times 10^{-5}$  M solution of **PtH** as shown in Figure 5. **PtH** is considered to be accommodated in a hydrophobic sphere of **P(Glu)-DDA** to avoid the solvent-induced quenching. Furthermore, a new

Figure 4. CD spectra of **P(Glu)-DDA** and **P(Glu)-DDA-PtH** (5:5:1) in methanol (**PtH** unit:  $5.0 \times 10^{-5}$  M) at 298 K.

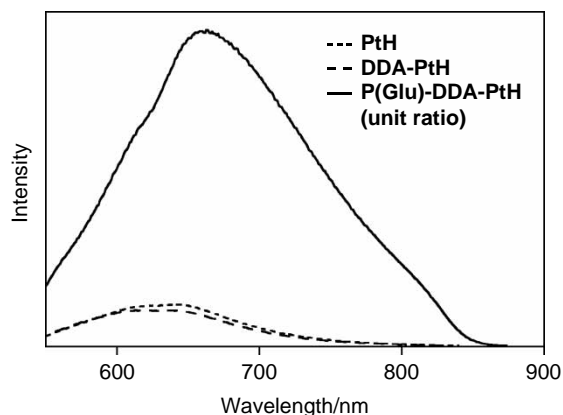


Figure 5. Emission spectra of **PtH**, **DDA-PtH** (5:1) and **P(Glu)-DDA-PtH** (5:5:1) in methanol (**PtH** unit:  $5.0 \times 10^{-5}$  M) at 298 K.

emission shoulder band was detected with an emission maximum at around 810 nm. This new emission band might be derived from the triplet metal-metal-to-ligand charge transfer ( $^3\text{MMLCT}$ ) excited state resulting from  $\text{Pt(II)}-\text{Pt(II)}$  and  $\pi-\pi$  interactions based on the aggregation of **PtH**. Such aggregation and induced emission were not observed only in the presence of 500 mol% amount of DDA bromide. Hydrophobic sphere-decorated **P(Glu)-DDA** along the backbone of anionic helical **P(Glu)** was allowed to serve as a polymeric spatially aligned scaffold for the accommodation and aggregation of cationic **PtH**.

**P(Glu)-DDA**-induced aggregation was also observed in the case of the platinum(II) complex **PtC<sub>12</sub>** having a dodecyl chain. In the UV-vis spectra of the complex of **P(Glu)-DDA** with **PtC<sub>12</sub>** (unit ratio, 5:1), the appearance of a new absorption band at around 500 nm with a shoulder band at around 600 nm was detected as shown in Figure 6. The absorption at  $>500$  nm is probably assignable to the

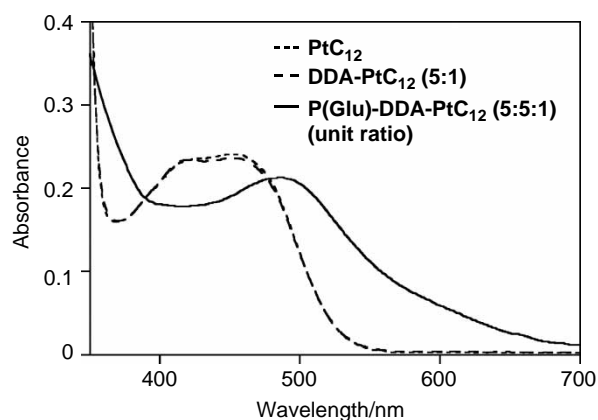


Figure 6. UV-vis spectra of **PtH**, **DDA-PtC<sub>12</sub>** (5:1) and **P(Glu)-DDA-PtC<sub>12</sub>** (5:5:1) in methanol (**PtC<sub>12</sub>** unit:  $5.0 \times 10^{-5}$  M) at 298 K.

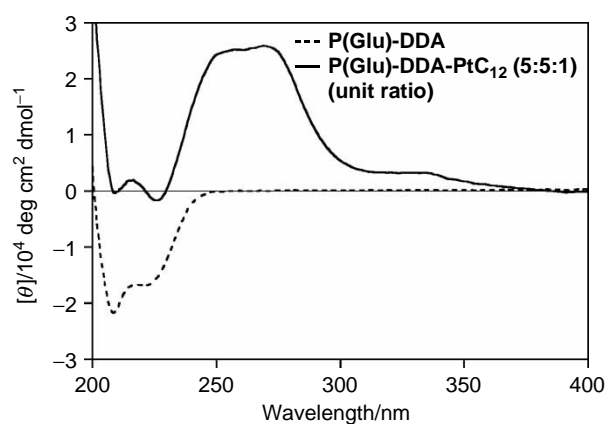


Figure 7. CD spectra of **P(Glu)-DDA** and **P(Glu)-DDA-PtC<sub>12</sub>** (5:5:1) in methanol (**PtC<sub>12</sub>** unit:  $5.0 \times 10^{-5}$  M) at 298 K.

$^3\text{MMLCT}$  transition based on the **P(Glu)-DDA**-induced aggregation. The accommodation of **PtC<sub>12</sub>** in **P(Glu)-DDA** was confirmed by the appearance of ICD at around 250–350 nm depending on the absorbance region of **PtC<sub>12</sub>** in the CD spectrum of the complex of **P(Glu)-DDA** with **PtC<sub>12</sub>** as shown in Figure 7.

In comparison to the emission of **PtH**, **PtC<sub>12</sub>** having a dodecyl chain ( $5.0 \times 10^{-5}$  M) exhibited a strong emission based on  $^3\text{MLCT}/^3\text{LLCT}$  at around 630 nm, even in the absence of **P(Glu)-DDA** as shown in Figure 8, indicating the self-aggregation through hydrophobic interaction between the dodecyl chains to escape the solvent-induced quenching. The difference of UV-vis spectra between the platinum(II) complexes **PtH** and **PtC<sub>12</sub>** might be due to the self-aggregation through hydrophobic interaction between the dodecyl chains of **PtC<sub>12</sub>**. It should be noted that the  $^3\text{MMLCT}$  emission at around 810 nm resulting from  $\text{Pt(II)}-\text{Pt(II)}$  and  $\pi-\pi$  interactions based on the aggregation

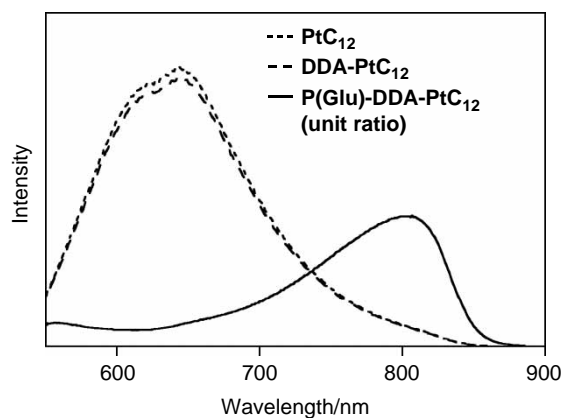


Figure 8. Emission spectra of **PtH**, **DDA-PtC<sub>12</sub>** (5:1) and **P(Glu)-DDA-PtC<sub>12</sub>** (5:5:1) in methanol (**PtC<sub>12</sub>** unit:  $5.0 \times 10^{-5}$  M) at 298 K.

of **PtC<sub>12</sub>** was observed with concomitant disappearance of the <sup>3</sup>MLCT/<sup>3</sup>LLCT emission by the addition of 500 mol% amount of **P(Glu)-DDA** to a methanol  $5.0 \times 10^{-5}$  M solution of **PtC<sub>12</sub>** (Figure 8). Such synergistic effect was not observed in the case of **PtH**. This result suggests the introduction of **PtC<sub>12</sub>** through hydrophobic interaction between the dodecyl chains and electrostatic interaction to arrange the platinum(II) terpyridyl moieties regularly into a hydrophobic sphere of **P(Glu)-DDA**. The dodecyl moiety of **PtC<sub>12</sub>** was found to play an important role in the aggregation of the platinum(II) terpyridyl moieties to induce Pt(II)–Pt(II) and  $\pi$ – $\pi$  interactions. Such aggregation and induced emission were not observed only in the presence of 500 mol% amount of DDA bromide.

### 3. Conclusion

The introduction of DDA cation as a cationic surfactant along the exterior of P(Glu) was demonstrated to afford **P(Glu)-DDA**, which was confirmed to form the  $\alpha$ -helical structure even in methanol. Hydrophobic sphere-decorated **P(Glu)-DDA** along the backbone of anionic helical P(Glu) was allowed to serve as a polymeric spatially aligned scaffold for the accommodation and aggregation of **PtC<sub>12</sub>**, wherein 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  $\pi$ – $\pi$  interactions. Studies on the application of polypeptide-induced metal ion aggregates including functional materials and catalysts are now in progress.

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