



## Controlled emission of platinum(II) terpyridyl complexes with poly-L-glutamic acid

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### ARTICLE INFO

#### Article history:

Received 9 June 2010

Received in revised form

21 July 2010

Accepted 27 July 2010

Available online 11 August 2010

#### Keywords:

Bioorganometallic chemistry

Poly-L-glutamic acid

Platinum(II) complex

Emission properties

Metal–metal interaction

### ABSTRACT

Poly-L-glutamic acid, P(Glu), bearing multiple negatively charged side chains served as a polymeric spatially aligned scaffold for the aggregation of positively charged platinum(II) complexes [Pt(trpy)C≡CR](OTf) (trpy = 2,2',6',2''-terpyridine; R = Ph (**PtH**), PhC<sub>12</sub>H<sub>25</sub>-p (**PtC<sub>12</sub>**)) through electrostatic interaction, resulting in tunable emission properties. **PtC<sub>12</sub>** was found to exhibit gradual increase in the emission intensity based on the triplet metal–metal-to–ligand charge transfer (<sup>3</sup>MMLCT) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) solution with concomitant decrease in the emission intensity based on the triplet metal-to–ligand charge transfer (<sup>3</sup>MLCT)/the triplet ligand-to–ligand charge transfer (<sup>3</sup>LLCT) as the amount of P(Glu) was increased. Such synergistic effect was not observed in the case of **PtH**, wherein the emission intensity based on <sup>3</sup>MLCT/<sup>3</sup>LLCT was increased by the increase in the amount of P(Glu), indicating that alkyl long chain of **PtC<sub>12</sub>** is considered to play an important role in the aggregation of the platinum(II) terpyridyl moieties to show Pt(II)–Pt(II) and π–π interactions.

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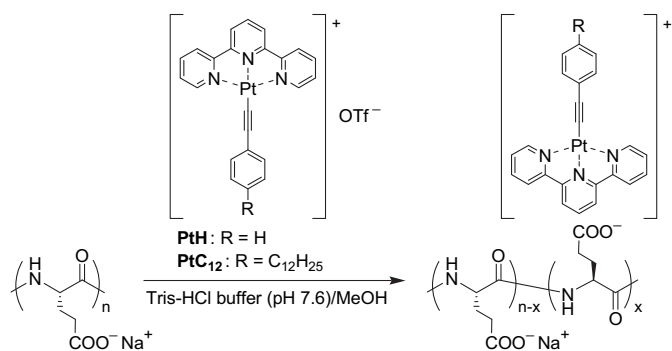
### 1. Introduction

Square-planar d<sup>8</sup> transition metal complexes possess the intriguing photophysical and photochemical properties. In particular, luminescent platinum(II) complexes with oligopyridine and cyclometalating 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 π–π interactions [1]. On the other hand, highly-ordered molecular assemblies are constructed in bio-systems to fulfill unique functions as observed in enzymes, receptors, etc. Introduction of functional complexes into highly-ordered biomolecules is considered to be a convenient approach to novel biomaterials, bio-inspired systems, etc. Recently, the field of bioorganometallic chemistry has drawn much attention and undergone rapid development [2]. Conjunction of organometallic compounds with biomolecules such as peptides and nucleobases is envisioned to afford such bioconjugates. Architectural control of molecular aggregation is of importance for the development of functional materials [3]. The utilization of polyelectrolytes has been recognized to be a reliable strategy for the assembly of oppositely-

charged functional groups along polyelectrolytes through electrostatic interaction [1m,1o,1r,4]. In a previous paper, redox-active ferrocenes bearing a long alkylene chain have been aggregated along the backbone of anionic double helical DNA, presenting a redox-active (outer) and hydrophobic (inner) spheres around the double helical core [5]. 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> aggregates [6]. 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 is envisioned to serve as a polymeric spatially aligned scaffold for the aggregation of positively charged organometallic compounds through electrostatic interaction. Anionic polyelectrolytes such as single-stranded nucleic acids, P(Glu), and poly(acrylic acid) have been demonstrated to induce the aggregation of the positively charged alkylplatinum(II) complexes, resulting in luminescence based on the metal–metal and π–π interactions [1m,1o,1r]. We have also embarked upon the controlled aggregation of cationic platinum(II) terpyridyl complexes with arylacetylide ligands spatially along the anionic α-helical P(Glu) to regulate the formation of the

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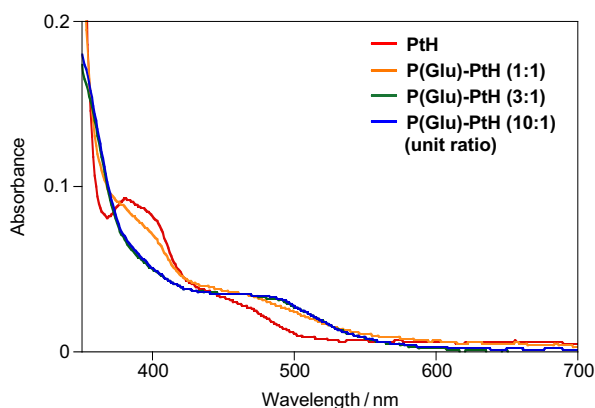


**Fig. 1.** The introduction of cationic platinum(II) terpyridyl complexes with arylacetylide ligands  $[\text{Pt}(\text{trpy})\text{C}\equiv\text{CR}](\text{OTf})$  ( $\text{trpy} = 2,2',6',2''$ -terpyridine;  $\text{R} = \text{Ph}$  (**PtH**),  $\text{PhC}_{12}\text{H}_{25-p}$  (**PtC<sub>12</sub>**)) into P(Glu).

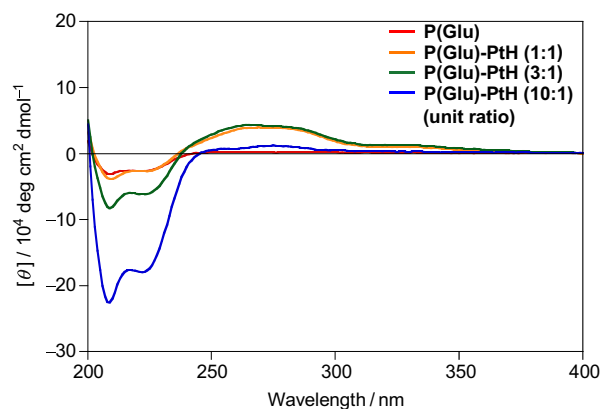
luminescent platinum(II) aggregates (Fig. 1). Herein, we report the effect of the alkyl chain of platinum(II) terpyridyl complexes with arylacetylide ligands in the formation of the platinum(II) aggregates accommodated in P(Glu) in a tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) solution to control emission properties.

## 2. Results and discussion

The aggregation of the cationic platinum(II) terpyridyl complexes with arylacetylide ligands  $[\text{Pt}(\text{trpy})\text{C}\equiv\text{CR}](\text{OTf})$  ( $\text{trpy} = 2,2',6',2''$ -terpyridine;  $\text{R} = \text{Ph}$  (**PtH**),  $\text{PhC}_{12}\text{H}_{25-p}$  (**PtC<sub>12</sub>**)) spatially along the anionic  $\alpha$ -helical P(Glu) was investigated by UV/vis spectroscopy (Fig. 2). The platinum(II) complex **PtH** showed an absorption band at around 450 nm, which probably originates from a mixed  $d\pi(\text{Pt}) \rightarrow \pi^*(\text{trpy})$  metal-to-ligand charge transfer (MLCT) and  $\pi(\text{alkynyl}) \rightarrow \pi^*(\text{trpy})$  ligand-to-ligand charge transfer (LLCT) transitions. The addition of 100 mol% amount (based on the Glu unit) of poly-L-glutamic acid sodium salt (P(Glu)) to a tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) solution of **PtH** led to the appearance of a new shoulder band at around 500 nm, and increase in the ratio of the Glu unit to **PtH** resulted in gradual increase in the peak in the UV/vis spectra ( $5.0 \times 10^{-5}$  M **PtH** unit) as shown in Fig. 2. By reference to previous works [1m,1q,1r,1s,1u], this new shoulder band might be assignable as a metal-metal-to-ligand charge transfer (MMLCT) transition. Circular dichroism (CD) spectrometry is a useful tool to determine an ordered structure in solution. An induced circular



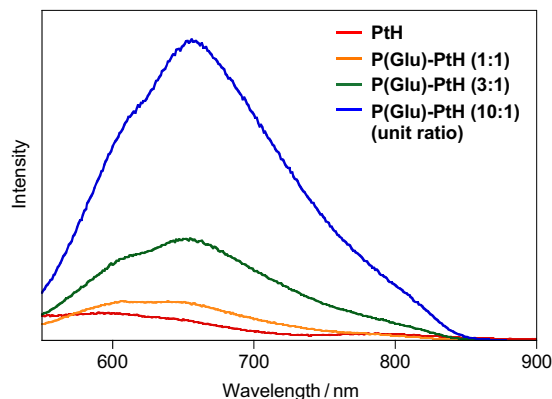
**Fig. 2.** UV/vis spectra of **PtH** ( $5.0 \times 10^{-5}$  M) in a tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) containing various amounts of P(Glu) (0.0, 0.5, 1.5, and  $5.0 \times 10^{-4}$  M Glu unit, respectively) at 298 K.



**Fig. 3.** CD spectra of P(Glu) ( $5.0 \times 10^{-5}$  M) and **PtH** ( $5.0 \times 10^{-5}$  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  $5.0 \times 10^{-4}$  M Glu unit, respectively) at 298 K.

dichroism (ICD) at around 250–350 nm based on the absorbance region of **PtH** was observed in the CD spectra of each mixture of P(Glu) and **PtH** (Fig. 3). These results suggest the aggregation of the cationic complex **PtH** spatially around the backbone of anionic P(Glu). Also, negative double minima at 209 and 221 nm indicate the preservation of an  $\alpha$ -helical structure. The electrostatic interactions between the cationic platinum(II) complexes and negatively charged side chains of P(Glu) are thought to stabilize the  $\alpha$ -helical structure by suppressing repulsion between negatively charged side chains.

**PtH** ( $5.0 \times 10^{-5}$  M) showed weak emission based on the triplet metal-to-ligand charge transfer ( $^3\text{MLCT}$ )/the triplet ligand-to-ligand charge transfer ( $^3\text{LLCT}$ ) at around 600 nm in a tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) solution probably due to solvent-induced quenching (Fig. 4). It is noteworthy mentioned that the addition of P(Glu) to the  $5.0 \times 10^{-5}$  M solution of **PtH** caused the increase in emission intensity. Increasing the ratio of the Glu unit to **PtH** led to gradual increase in the emission intensity as shown in Fig. 4. **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  $[\text{Pt}(\text{trpy})\text{C}\equiv\text{CR}]^+$  have been reported to show the triplet metal-metal-to-ligand charge transfer ( $^3\text{MMLCT}$ ) emission band at around 800 nm resulting from Pt(II)–Pt(II) and  $\pi$ – $\pi$  interactions based on the aggregation



**Fig. 4.** Emission spectra ( $\lambda_{\text{ex}} = 350$  nm) of **PtH** ( $5.0 \times 10^{-5}$  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  $5.0 \times 10^{-4}$  M Glu unit, respectively) at 298 K.

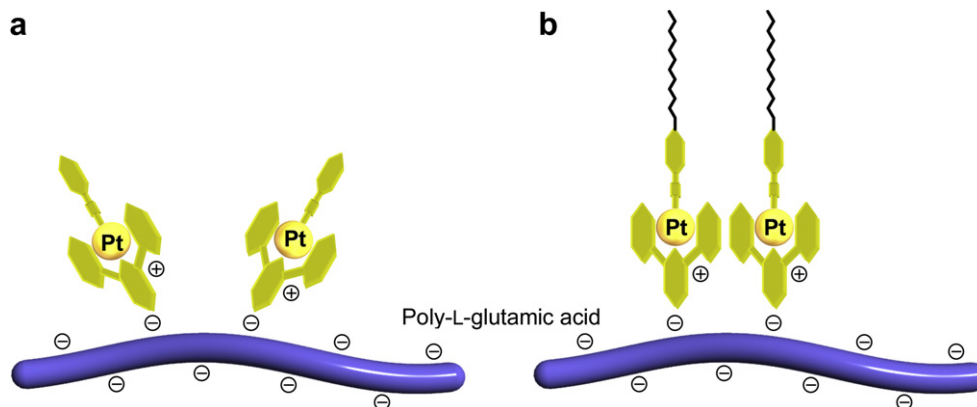


Fig. 5. Schematic representation of P(Glu)-induced aggregation for (a) **PtH** and (b) **PtC<sub>12</sub>**.

[1m,1q,1r,1s,1u]. The new emission band at around 820 nm might be derived from the <sup>3</sup>MMLCT excited state resulting from Pt(II)–Pt(II) and  $\pi$ – $\pi$  interactions based on the aggregation of **PtH**. P(Glu) bearing multiple negatively charged side chains was found to serve as a polymeric spatially aligned scaffold for the accommodation and aggregation of cationic **PtH** (Fig. 5a).

In comparison to the emission of **PtH**, the platinum(II) complex **PtC<sub>12</sub>** having a dodecyl chain ( $5.0 \times 10^{-5}$  M) exhibited a strong emission based on <sup>3</sup>MLCT/<sup>3</sup>LLCT at around 650 nm even in the absence of the P(Glu) as shown in Fig. 6. The platinum(II) complex **PtC<sub>12</sub>** could assemble easily in a polar environment. This result suggests the self-aggregation through hydrophobic interaction between dodecyl chains to avoid the solvent effect. Interestingly, the <sup>3</sup>MMLCT emission at around 820 nm resulting from Pt(II)–Pt(II) and  $\pi$ – $\pi$  interactions based on the aggregation 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 100 mol% amount of P(Glu) to a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) solution of **PtC<sub>12</sub>** (Fig. 6). This result indicates hydrophobic interaction between 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) (Fig. 5b). 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. Furthermore, increase in the ratio of P(Glu) caused gradual increase in the <sup>3</sup>MMLCT emission intensity with concomitant decrease in the <sup>3</sup>MLCT/<sup>3</sup>LLCT emission intensity. High loading of P(Glu) per **PtC<sub>12</sub>** would lead to the accommodation and aggregation of cationic **PtC<sub>12</sub>** in a hydrophobic sphere of P(Glu). The aggregation of **PtC<sub>12</sub>** around the backbone of  $\alpha$ -helical P(Glu) was also confirmed by UV/vis and CD spectra. The appearance of a new absorption band at around 500 nm with a shoulder band at around 600 nm was observed by the addition of 100 mol% amount (based on the Glu unit) of P(Glu) to a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) solution of **PtC<sub>12</sub>** in the UV/vis spectra ( $5.0 \times 10^{-5}$  M **PtC<sub>12</sub>** unit) as shown in Fig. 7. The absorption at >500 nm is probably assignable to the MMLCT transition based on the P(Glu) induced aggregation. Furthermore, increase in the ratio of the Glu unit to **PtC<sub>12</sub>** resulted in gradual increase in the peak. The absorption spectrum was changed largely between 1:1 and 3:1 of **P(Glu)**–**PtC<sub>12</sub>**. High loading of P(Glu) per **PtC<sub>12</sub>** would lead to the accommodation and aggregation of cationic **PtC<sub>12</sub>** in a hydrophobic sphere of P(Glu), resulting in the change of the absorption spectrum. The accommodation of **PtC<sub>12</sub>** in a hydrophobic sphere of P(Glu) was supported by the appearance of an ICD at around 250–350 nm based on the absorbance region of **PtC<sub>12</sub>** in the CD spectra of **PtC<sub>12</sub>** complex in the presence of P(Glu) as shown in Fig. 8.

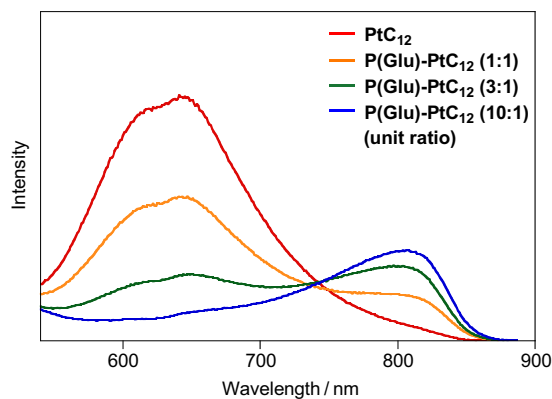


Fig. 6. Emission spectra ( $\lambda_{\text{ex}} = 350$  nm) of **PtC<sub>12</sub>** ( $5.0 \times 10^{-5}$  M) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) containing various amounts of P(Glu) (0.0, 0.5, 1.5, and  $5.0 \times 10^{-4}$  M Glu unit, respectively) at 298 K.

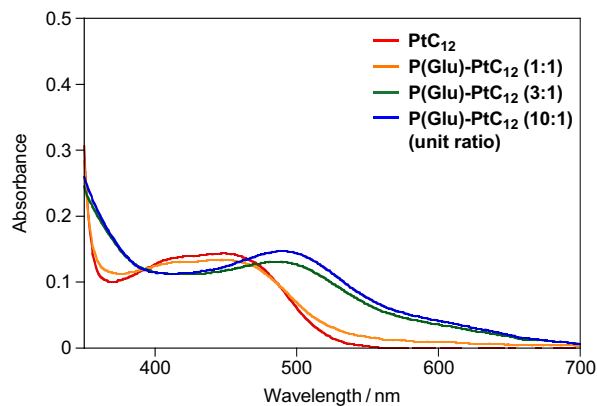
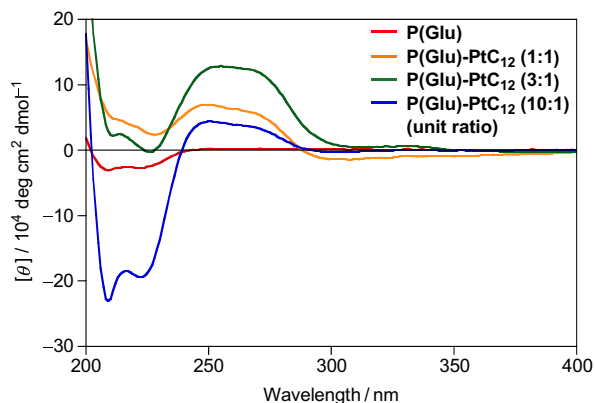


Fig. 7. UV/vis spectra of **PtC<sub>12</sub>** ( $5.0 \times 10^{-5}$  M) in a tris/HCl buffer (pH 7.6)/MeOH (v/v = 1/14) containing various amounts of P(Glu) (0.0, 0.5, 1.5, and  $5.0 \times 10^{-4}$  M Glu unit, respectively) at 298 K.



**Fig. 8.** CD spectra of P(Glu) ( $5.0 \times 10^{-5}$  M) and PtC<sub>12</sub> ( $5.0 \times 10^{-5}$  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  $5.0 \times 10^{-4}$  M Glu unit, respectively) at 298 K.

### 3. Conclusion

Tunable emission properties of positively charged platinum(II) terpyridyl complexes with arylacetylide ligands were demonstrated by use of poly-L-glutamic acid, P(Glu), bearing multiple negatively charged side chains as a polymeric spatially aligned scaffold for the aggregation of the platinum(II) complexes 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 Pt(II)–Pt(II) and  $\pi$ – $\pi$  interactions. The architectural control of molecular assemblies utilizing biomolecules is envisioned to be a useful approach to artificial highly-ordered bio-organometallic systems. Studies on the application of polypeptide induced metal ion aggregates including functional materials and catalysts are now in progress.

### 4. Experimental

#### 4.1. General materials and experimental procedures

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Poly-L-glutamic acid sodium salt with mol. wt. >8000 was obtained from PEPTIDE INSTITUTE, INC. [Pt(trpy)Cl](OTf) [1e] and [Pt(trpy)C≡CPh](OTf) PtH [1u] were prepared by the literature methods. All manipulations were carried out under argon. <sup>1</sup>H NMR spectra were recorded on a JNM-ECS 400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS DX-303 spectrometer.

#### 4.2. Synthesis of the platinum(II) complex PtC<sub>12</sub>

To a mixture of [Pt(trpy)Cl](OTf) (62.9 mg, 0.103 mmol), CuI (2.20 mg, 11.6  $\mu$ mol), and triethylamine (200  $\mu$ L, 1.4 mmol) was dropwise added 1-dodecyl-4-ethynylbenzene (110 mg, 0.407 mmol) in dichloromethane (5 mL) under argon at room temperature. The mixture was stirred under argon at room temperature for 22 h. The volume of the solvent was reduced. The precipitated product was collected by filtration. Subsequent recrystallization by vapor diffusion of ether into a methanol solution gave PtC<sub>12</sub> as dark purple crystals.

**PtC<sub>12</sub>:** yield 70%; IR (KBr) 2120 (C≡C)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  8.76 (d with <sup>195</sup>Pt satellites, 2H,  $J = 5.6$  Hz), 8.17 (t, 2H,  $J = 7.8$  Hz), 8.16 (t, 1H,  $J = 7.8$  Hz), 8.01 (d, 2H,  $J = 7.8$  Hz), 8.00 (d,

2H,  $J = 7.8$  Hz), 7.58–7.54 (m, 2H), 7.21 (d, 2H,  $J = 8.4$  Hz), 7.17 (d, 2H,  $J = 8.4$  Hz), 2.66 (t, 2H,  $J = 7.8$  Hz), 1.69–1.62 (m, 2H), 1.39–1.25 (m, 18H), 0.89 (t, 3H,  $J = 6.9$  Hz); HRMS (FAB)  $m/z$  calcd for C<sub>35</sub>H<sub>40</sub>N<sub>3</sub>Pt ([M – OTf]<sup>+</sup>), 697.2870; found, 697.2880; Anal. Calcd. for C<sub>36</sub>H<sub>40</sub>N<sub>3</sub>O<sub>3</sub>F<sub>3</sub>Spt: C, 51.06; H, 4.76; N, 4.96. Found: C, 50.79; H, 4.69; N, 5.09.

#### 4.3. General procedure of UV/vis measurement

UV/vis spectra were obtained using a Hitachi U-3500 spectrophotometer in a deaerated tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) solution with the concentration  $5.0 \times 10^{-5}$  M for the platinum(II) complex under argon at 298 K. UV/vis spectra were measured using 1-cm pathlength quartz cuvettes.

#### 4.4. General procedure of CD measurement

CD spectra were recorded using a JASCO J-720 spectropolarimeter in a deaerated tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) solution with the concentration  $5.0 \times 10^{-5}$  M for the platinum(II) complex under argon at 298 K. CD spectra were measured using 1-cm pathlength quartz cuvettes.

#### 4.5. General procedure of emission measurement

Emission spectra were measured using a Shimadzu RF-5300PC spectrofluorophotometer in a deaerated tris/HCl buffer (pH 7.6)/MeOH ( $v/v = 1/14$ ) solution with the concentration  $5.0 \times 10^{-5}$  M for the platinum(II) complex under argon at 298 K. Emission spectra were measured using 1-cm pathlength quartz cuvettes.

### Acknowledgement

This work was supported by Grant-in-Aids for Science Research on Priority Areas (No. 20036034) and Innovative Areas (No. 21111512) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Thanks are also due to the Analytical Center, Graduate School of Engineering, Osaka University, for the use of the CD instrument.

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