

Synthesis and photophysical characterization of ruthenium(II) and platinum(II) complexes with bis-pyridylethynyl-phenanthroline ligands as a metalloligand

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Abstract

Novel ruthenium complexes $\text{Ru(L)(bpy)}_2(\text{PF}_6)_2$ and platinum organometallic complexes $\text{Pt(L)(-}\equiv\text{-C}_6\text{H}_5\text{CH}_3)_2$ with bis-(pyridinyl)ethynyl-phenanthrolines ($\text{L} =$ 3,8-bis[2-(3-pyridinyl)ethynyl]-1,10-phenanthroline or 3,8-bis[2-(4-pyridinyl)ethynyl]-1,10-phenanthroline) that function as metalloligands by extra pyridyl units have been prepared using respective synthetic methods. These complexes have broad absorption bands assignable to the MLCT band as the main contributing factor in the 400-550 nm wavelength area. Furthermore, these complexes show phosphorescence centered around 680 nm upon excitation at 425 nm. These emissions were assigned to a triplet MLCT-based luminescence for ruthenium complexes, while a triplet MLCT as the main element, including the interligand charge transfer as the minor element, was assigned for platinum organometallic complexes. The quantum yields of the emission of the present ruthenium complexes were relatively high, and these complexes are exactly phosphorescent dyes, although the emission intensities of the platinum complexes are poor. These two types of complexes are capable of selective photophysical detection of some metal ions and can serve as metalloligands in the construction of supramolecular metallocycles.

Keywords: Ruthenium; Platinum; Phosphorescence; Metalloligand

Introduction

Construction of supramolecular metal complexes with many types of pyridyl ligands has been extensively investigated in the past few decades. Their supramolecular complexes have potential applications in the fields of sensing and catalysts by virtue of their particularly interesting properties of internal space [1-7]. Extensive studies of supramolecular macrocycles with platinum(II) and palladium(II) complexes have been carried out by Stang et al.[1, 2] and Fujita et al. [3-5] in the past two decades. Photosensing studies of supramolecular platinum(II) complexes with a hydrophobic cavity have been an active area of research in recent years [1-3]. As a part of this research trend, we have recently reported the formation of supramolecular macrocycles with two types of platinum(II) complexes, which are composed of platinum(II) bipyridine organometallic complexes including 4-(4-ethynyl-phenylethynyl)-pyridine and Pt(bis-(diphenylphosphino)-propane)(OTf)₂, in solution [8]. These new platinum organometallic compounds are among the so-called metalloligands, and the study of supramolecular macrocycles with many types of metalloligands has attracted particular interest in recent years [2, 9, 10].

In contrast, many kinds of ruthenium(II) polypyridyl complexes have long been studied as some of the most important compounds in photophysical chemistry [11]. Furthermore, the photophysical study of platinum organometallic complexes including two ethynylaryl ligands with bipyridine derivatives has been reported by several groups in the recent past, owing to a characteristic phosphorescence caused by the heavy atom effect of the platinum atom on these complexes [12-15]. Moreover, the photophysical study of these platinum(II) organometallic complexes has recently expanded to some characteristic chromisms with vapor of specific volatile organic compounds (vapochromism), heating (thermochromism), and mechanical force (mechanochromism) [16,17].

We therefore became interested in the photophysical property of new ruthenium(II) polypyridyl complexes and platinum(II) organometallics with phenanthroline ligand including two extra pyridyl units as metalloligands (Fig. 1) because these complexes have the potential ability to serve as building blocks in the construction of photofunctional supramolecular complexes and the capability of photophysical sensing for specific metal ions accompanied by the coordination to free pyridyl units.

We report herein the preparation and characterization of novel ruthenium(II) polypyridyl and platinum(II) organometallic complexes with two types of bis-(pyridinyl)ethynyl-phenanthrolines, which are represented as $\text{Ru}(\text{L})(\text{bpy})_2(\text{PF}_6)_2$ (**Ru1** and **Ru2**) and $\text{Pt}(\text{L})(-\text{C}\equiv\text{C}_6\text{H}_5\text{CH}_3)_2$ (**Pt1** and **Pt2**) ($\text{L} = 3,8\text{-bis}[2\text{-(3-pyridinyl)ethynyl}]\text{-1,10-phenanthroline}$ (**L1**) or $3,8\text{-bis}[2\text{-(4-pyridinyl)ethynyl}]\text{-1,10-phenanthroline}$ (**L2**), as shown in Fig. 1. These complexes show phosphorescence centered around 680 nm upon the excitation at 425 nm. However, the emission quantum yields between ruthenium and platinum complexes in the solution are very different. The emission intensities of the present ruthenium complexes are high enough to make these complexes candidate for phosphorescent dye, while those of platinum complexes are poor.

Experimental section

Material and measurements

All chemicals used for synthesis were purchased from Aldrich or TCI and used without further purification. All reactions were carried out under an argon atmosphere. Solvents were freshly distilled according to standard procedures. The 3,8-diethynylphenanthroline were synthesized by the similar method of Ziessel et al. [18]. The Pt(COD)(\equiv -C₆H₅CH₃)₂ (COD = 1,5-cyclooctadiene) and Ru(bpy)₂Cl₂ (bpy = 2,2'-bipyridine) were synthesized by the standard method. The characterization of the novel ruthenium and platinum complexes has been done by IR, ¹H NMR, UV-Vis absorption, emission spectroscopy and elemental analyses. Elemental analyses were performed for C, H, and N elements on a PerkinElmer 2400II CHNS/O full-automatic analyzer. IR spectra were obtained on a JASCO FT/IR 460 spectrometer using the KBr-pellet method. The ¹H NMR spectra were recorded with a Bruker AVANCE NMR spectrometer (400MHz) at room temperature and the chemical shifts were referenced to CDCl₃ (7.26 ppm) or CD₂Cl₂ (5.32 ppm) or CD₃CN (1.94 ppm). ESI mass spectra of ruthenium complexes were obtained in positive-ion mode with a Synapt G2 HDMS mass spectrometer (waters). The samples employed for spectral measurements were prepared in an acetonitrile (HPLC grade). UV-Vis spectra were recorded on a SHIMADZU UV-1800 spectrophotometer in CH₂Cl₂ (emission spectroscopic grade) or CH₃CN (emission spectroscopic grade) at room temperature. The corrected emission spectra were measured with a HAMAMATSU C7473 photonic multi-channel analyzer, and excitation spectra were recorded on a HITACHI F-2500 fluorescence spectrophotometer. Emission spectra for quantum yield measurement at room temperature were measured in a degassed acetonitrile by argon bubbling (over 30 min) upon excitation at 425 nm. The quantum yield of emission (ϕ) was determined by comparison with the value for [Ru(bpy)₃](PF₆)₂ (ϕ_{em} = 0.095) [19].

Preparation of 3,8-bis[2-(3-pyridinyl)ethynyl]-1,10-phenanthroline (**L1**)

Ligand **L1** was prepared by the similar procedure of Stang et al. [20]. A flask was charged with 3,8-diethynylphenanthroline (229 mg, 1.0 mmol) and 3-iodopyridine (472 mg, 2.3 mmol), and dissolved with the mixture solution of dry THF (90 ml) and triethylamine (9ml). The Pd(PPh₃)₄ (116 mg, 0.10 mmol) and CuI (30 mg, 0.16 mmol) were added to the flask. After the mixture was stirred at 60 °C for 7 h, THF and triethylamine were removed by reduced pressure. The residue was dissolved with CH₂Cl₂-MeOH (95:5 ml) and added to an aqueous solution of KCN (1.0 g in 50 ml). After the solution was treated with the ultrasonic sound for 1 h, the organic phase was separated and removed by evaporation with evaporator. The residue was further purified on SiO₂ column chromatography with CH₂Cl₂-MeOH (95:5 to 90:10, gradually) as eluent. Yellow powder was obtained and dried at 50 °C under vacuum for 3 hr. Yield: 320 mg (83 %).

Anal. Calcd for C₂₆H₁₄N₂·0.5H₂O: C, 79.9; H, 3.9; N, 14.3. Found: C, 80.4; H, 4.1; N, 14.0%. IR (cm⁻¹) ν(C≡C): 2215. UV/VIS (CH₂Cl₂): λ_{abs} nm (ε × 10⁻⁴) 356 (7.4), 341 (8.3), 285 (6.9). ¹H NMR (CDCl₃, ppm): 9.30 (d, J = 2.0 Hz, 2H, Phen-H2 and -H9), 8.87 (d, J = 2.0 Hz, 2H, Py-H2), 8.62 (dd, J = 4.9 and 2.0 Hz, 2H, Py-H4), 8.42 (d, J = 2.0 Hz, 2H, Phen-H4 and -H7), 7.91 (dt, J = 7.9, 2.0, and 2.0 Hz, 2H, Py-H6) 7.83 (s, 2H, Phen-H5 and -H6), 7.35 (dd, J = 7.9 and 4.9 Hz, 2H, Py-H5).

Preparation of 3,8-bis[2-(4-pyridinyl)ethynyl]-1,10-phenanthroline (**L2**)

Ligand **L2** was prepared with double volume of **L1** except for the use of 4-iodopyridine according to same procedure reported by Stang et al. [20]. Yield: 650 mg (85 %).

Anal. Calcd for C₂₆H₁₄N₂·0.5H₂O: C, 79.9; H, 3.9; N, 14.3. Found: C, 79.6; H, 3.9; N, 13.9%. IR (cm⁻¹) ν(C≡C): 2218. UV/VIS (CH₂Cl₂): λ_{abs} nm (ε × 10⁻⁴) 356 (5.8), 339 (6.9), 284 (6.4) ¹H NMR (CDCl₃, ppm): 9.30 (d, J = 2.0 Hz, 2H, Phen-H2 and -H9), 8.68 (d, J = 6.0 Hz, 4H, Py-H2 and -H6), 8.44 (d, J = 2.0 Hz, 2H, Phen-H4 and -H7), 7.83 (s, 2H, Phen-H5 and -H6), 7.48 (d, J = 6.0 Hz, 4H, Py-H3 and -H5).

Preparation of [Ru(**L1**)(bpy)₂](PF₆)₂ (**Ru1**)

Ruthenium complex $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (520 mg, 1.0 mmol) was dissolved in a mixture solution of EtOH (140 ml) - H_2O (14 ml) under Ar. To the solution was added **L1** (384 mg, 1.0 mmol) and stirred at 90°C for 22 h. After cooling the reacted solution, water (10 ml) was added to the solution and the ethanol was removed by an evaporator under reduced pressure. The residual solution was filtered through the filter paper, and the filtrate was added to the water solution (100 ml) containing NH_4PF_6 (1630 mg, 10 mmol). The brown precipitate was collected by filtration with a suction filter, and the residue was further purified on ODS column chromatography with CH_3CN containing NH_4PF_6 (8mg per 100ml) as eluent. Dark red powder was washed with water (30 ml), ethanol (5ml) and dried at 50°C under vacuum for 3 hr. Yield: 746 mg (69 %).

Anal. Calcd for $\text{C}_{46}\text{H}_{30}\text{N}_8\text{P}_2\text{F}_{12}\text{Ru}_1\cdot\text{H}_6\text{O}_3$: C, 48.5; H, 3.4; N, 9.8. Found: C, 48.3; H, 3.1; N, 10.0%. Positive ESI-MS: ion at m/z 398.09 (M^{2+} , 100 %). FT-IR (KBr, cm^{-1}) $\nu(\text{C}\equiv\text{C})$: 2224. UV/VIS (CH_3CN): UV/VIS (CH_3CN): λ_{abs} nm ($\epsilon \times 10^{-4}$) 487 (0.9), 439 (1.4), 355 (6.3), 287 (10.6). $^1\text{H-NMR}$ (CD_3CN , ppm): 8.76 (d, $J = 1.8$ Hz, 2H, Phen-H4 and -H7), 8.73 (d, $J = 1.5$ Hz, 2H, Py-H2), 8.61 (dd, $J = 5.0$ and 1.5 Hz, 2H, Py-H4), 8.54 (d, $J = 8.0$ Hz, 2H, bpy-H6), 8.50 (d, $J = 8.0$ Hz, 2H, bpy-H6'), 8.27 (s, 2H, Phen-H5 and -H6), 8.22 (d, $J = 1.8$ Hz, 2H, Phen-H2 and -H9), 8.12 (td, $J = 8.0$, 8.0 , and 2.0 Hz, 2H, bpy-H5), 8.03 (td, $J = 8.0$, 8.0 , and 2.0 Hz, 2H, bpy-H5'), 7.88 (dt, $J = 8.3$, 1.5 , and 1.5 Hz, 2H, Py-H6), 7.81 (d, $J = 6.0$ Hz, 2H, bpy-H3), 7.63 (d, $J = 6.0$ Hz, 2H, bpy-H3'), 7.46 (ddd, $J = 8.0$, 6.0 , and 2.0 Hz, 2H, bpy-H4), 7.41 (ddd, $J = 8.3$, 5.0 , and 1.5 Hz, 2H, Py-H5), 7.27 (ddd, $J = 8.0$, 6.0 , and 2.0 Hz, 2H, bpy-H4').

Preparation of $[\text{Ru}(\text{L2})(\text{bpy})_2](\text{PF}_6)_2$ (**Ru2**)

The complex **Ru2** was prepared by the same procedure of **Ru1** except for the use of the ligand **L2**. Yield: 775 mg (71 %).

Anal. Calcd for $\text{C}_{46}\text{H}_{30}\text{N}_8\text{P}_2\text{F}_{12}\text{Ru}_1\cdot\text{H}_6\text{O}_3$: C, 48.5; H, 3.4; N, 9.8. Found: C, 48.6; H, 3.4; N, 9.9%. FT-IR (KBr, cm^{-1}) $\nu(\text{C}\equiv\text{C})$: 2224. UV/VIS (CH_3CN): λ_{abs} nm ($\epsilon \times 10^{-4}$) 492 (0.8), 433 (1.47), 348 (5.8), 286 (10.9). $^1\text{H-NMR}$ (CD_3CN , ppm): 8.79 (d, $J = 1.7$ Hz, 2H, Phen-H4 and -H7), 8.64 (dd, $J = 4.5$ and 1.6 Hz, 4H, Py-H2 and -H6), 8.53 (d, $J = 8.0$ Hz, 2H, bpy-H6), 8.51 (d, $J = 8.0$ Hz, 2H, bpy-H6'), 8.28 (s, 2H, Phen-H5 and -H6), 8.25 (d, $J = 1.7$ Hz, 2H, Phen-H2 and -H9), 8.10 (td, $J =$

8.0, 8.0, and 1.5 Hz, 2H, bpy-H5), 8.03 (td, J = 8.0, 8.0, and 1.5 Hz, 2H, bpy-H5'), 7.80 (d, J = 5.0 Hz, 2H, bpy-H3), 7.62 (d, J = 5.0 Hz, 2H, bpy-H3'), 7.45 (ddd, J = 8.0, 5.0, and 1.5 Hz, 2H, bpy-H4), 7.43 (dd, J = 4.5, and 1.6 Hz, 4H, Py-3H and -H5), 7.26 (ddd, J = 8.0, 5.0, and 1.5 Hz, 2H, bpy-H4').

Preparation of Pt(**L1**)($\equiv\text{-C}_6\text{H}_5\text{CH}_3$)₂ (**Pt1**)

Platinum complex Pt(COD)($\equiv\text{-C}_6\text{H}_5\text{CH}_3$)₂ (180 mg, 0.34 mmol) and ligand **L1** (130 mg, 0.34 mmol) were dissolved in CH₂Cl₂ (20 ml) under Ar. To the solution further was added CH₃CN (80 ml) and stirred at 35 °C for 4 days. After cooling, the reacted solution was filtered through the filter paper and the solvents of the filtrate were removed by an evaporator under reduced pressure. To the residue was added CH₂Cl₂ (10 ml) to dissolve some impurities, and the precipitate was obtained by filtration with a suction filter. Red powder was washed with ether (10 ml) and dried at 50 °C under vacuum for 3 h. Yield: 217 mg (79 %).

Anal. Calcd for C₄₄H₂₈N₄Pt₁·0.5H₂O: C, 64.7; H, 3.6; N, 6.9. Found: C, 64.8; H, 3.6; N, 6.8%.

FT-IR (KBr, cm⁻¹) $\nu(\text{C}\equiv\text{C})$: 2113, 2215. UV/VIS (CH₂Cl₂): λ_{abs} nm ($\epsilon \times 10^{-4}$) 451 (0.48), 380 (4.3), 363 (4.4), 336 (3.9), 285 (6.0), 271 (6.1). ¹H-NMR (CD₂Cl₂, ppm): 9.98 (d, J = 1.8 Hz, 2H, Phen-H2 and -H9), 8.79 (broad s, 2H, Py-H2), 8.71 (d, J = 1.8 Hz, 2H, Phen-H4 and -H7), 8.61 (m, 2H, Py-H4), 8.01 (s, 2H, Phen-H5 and -H6), 7.85 (m, 2H, Py-H6), 7.46 (d, J = 7.2 Hz, 4H, Tolyl-H3 and -H5), 7.34 (m, 2H, Py-H5), 7.16 (d, J = 7.2 Hz, 4H, Tolyl-H2 and -H6), 2.39 (s, 6H, -CH₃).

Preparation of Pt(**L2**)($\equiv\text{-C}_6\text{H}_5\text{CH}_3$)₂ (**Pt2**)

The complex **Pt2** was prepared by the same procedure of **Pt1** except for the use of the ligand **L2**.

Yield: 180 mg (66 %).

Anal. Calcd for C₄₄H₂₈N₄Pt₁·1.0H₂O: C, 64.0; H, 3.7; N, 6.8. Found: C, 63.8; H, 3.5; N, 6.7%.

FT-IR (KBr, cm⁻¹) $\nu(\text{C}\equiv\text{C})$: 2113, 2219. UV/VIS (CH₂Cl₂): λ_{abs} nm ($\epsilon \times 10^{-4}$) 446 (0.52), 371 (4.6), 341 (5.8), 280 (7.3). ¹H-NMR (CD₂Cl₂, ppm): 9.85 (d, J = 1.8 Hz, 2H, Phen-H2 and -H9), 8.65 (d, J = 1.8 Hz, 2H, Phen-H4 and -H7), 8.62 (d, J = 4.6 Hz, 4H, Py-H2 and -H6), 7.98 (s, 2H, Phen-H5

and -H6), 7.43 (d, $J = 8.0$ Hz, 4H, Toly-H3 and -H5), 7.35 (d, $J = 4.6$ Hz, 4H, Py-H3 and -H5), 7.15 (d, $J = 8.0$ Hz, 4H, Toly-H2 and -H6), 2.40 (s, 6H, -CH₃).

Results and discussion

Synthesis and characterization

Phenanthroline ligands shown in Fig. 1, **L1** and **L2**, which have two extra pyridine units as the function of the metalloligand, were prepared with the usual cross-coupling reaction by a procedure similar to **L2** synthesis of Stang's group [20] and were obtained in good yields (**L1**: 83 %, **L2**: 85 %). The ruthenium(II) polypyridyl complexes, **Ru1** and **Ru2** (Fig. 1), were prepared by a method similar to that described in our recent report [21]. The preparation of platinum complexes, **Pt1** or **Pt2** (Fig. 1), was performed with the ligand exchange reaction between the COD of $\text{Pt}(\text{COD})(-\text{C}\equiv\text{C}_6\text{H}_5\text{CH}_3)_2$ (COD = 1,5-cyclooctadiene) and the respective phenanthroline, **L1** or **L2**, because the platinum complex, $\text{Pt}(3,8\text{-diethynylphenanthroline})\text{Cl}_2$, was hardly dissolved in common organic solvents. These novel compounds have been characterized by ^1H -NMR, IR, and elemental analyses.

IR spectral data of novel platinum complexes indicate two characteristic $\nu(\text{C}\equiv\text{C})$ bands at 2113 cm^{-1} and around 2220 cm^{-1} (**Pt1**: 2215 cm^{-1} , **Pt2**: 2219 cm^{-1}), while those of the ruthenium complexes and free ligands showed only one $\nu(\text{C}\equiv\text{C})$ band, assignable to the ethynyl substituent in the respective phenanthroline ligands around $2215\text{-}2224\text{ cm}^{-1}$. On the other hand, the precursor platinum complex $\text{Pt}(\text{COD})(-\text{C}\equiv\text{C}_6\text{H}_5\text{CH}_3)_2$ exhibits the $\nu(\text{C}\equiv\text{C})$ stretching band at 2113 cm^{-1} . These data clearly demonstrate that the $\nu(\text{C}\equiv\text{C})$ band at 2113 cm^{-1} of respective platinum complexes is derived from the η^1 coordination of σ -bonding (Pt-C \equiv C bond) between platinum atom and two tolylethynyl ligands. Furthermore, this $\nu(\text{C}\equiv\text{C})$ band assigned to the Pt-C \equiv C bond of the present platinum complexes is almost consistent with that (2110 cm^{-1}) of the previous reported platinum complex $\text{Pt}(\text{phen})(-\text{C}\equiv\text{C}_6\text{H}_5\text{CH}_3)_2$ [12]. Then, on the present platinum complexes, the simple coordination to the platinum center with two nitrogen atoms of the phenanthroline ring in **L1** and **L2** is reasonable, and the η^2 coordination to the metal center with the ethynyl bond in **L1** and **L2** under the ligand exchange reaction is excluded.

Coordination of the phenanthroline ligands to the metal center in **L1** and **L2** on the present complexes is further supported by the ^1H -NMR measurement data. The signal data of chemical shifts

for phenanthroline ligands on the present six compounds are listed in Table 1. The signals assignable to the phenanthroline-H2 and -H9 protons on the platinum complexes **Pt1** and **Pt2** clearly showed downfield shifts of more than 0.5 ppm compared with the signals of phenanthroline ligands **L1** and **L2**, while the signals assignable to the same protons on the ruthenium complexes **Ru1** and **Ru2** were shifted upfield more than 1.0 ppm because of strong π -back donation effects. On the other hand, the chemical shifts assignable to the pyridine-H2 and -H6 protons in **L1** or **L2**, which are the nearest-neighbor protons of the nitrogen atom in the pyridyl ring, changed only slightly (by less than 0.1 ppm) upon coordination to the metal center in both ruthenium and platinum complexes. This variation of their chemical shifts could be also explained by the simple coordination with two nitrogen atoms of the phenanthroline ring to the metal center and the absence of coordination with those of the pyridine rings in these complexes.

Additionally, the ESI mass spectra of ruthenium complexes, **Ru1** and **Ru2**, mainly showed the molecular ion $[\text{Ru}(\text{bpy})(\text{L})]^{2+}$ ($\text{L} = \text{L1}$ or **L2**) at m/z 392, with a satisfactory isotopic matching to the simulated pattern of the estimated cation.

Photophysical properties

Figure 2 shows the absorption spectra of ruthenium complexes, **Ru1** and **Ru2**, in CH_3CN , while the absorption spectra of platinum complexes, **Pt1** and **Pt2**, and of free phenanthrolines, **L1** and **L2**, in CH_2Cl_2 are shown in Fig. 3. Both metal complexes have a broad absorption band in the 400-550 nm wavelength area. These bands are assigned to the MLCT band for ruthenium complexes and to the mixed transition of both the MLCT as the main contributing factor and the interligand CT between the phenanthroline and tolylethynyl ligands as minor contributing factors for platinum complexes; these findings are consistent with those of previous reports on ruthenium(II) polypyridyl complexes with many types of bipyridine and/or phenanthroline derivatives [21, 22] and on platinum bipyridine organometallics including two arylacetylide ligands [11-15], respectively. The molar extinction coefficients for the absorption of ruthenium complexes are higher than those of platinum complexes in the 400-550 nm region because the present ruthenium complexes have not only a phenanthroline ligand but also two bipyridine ligands, and two types of MLCT bands are overlapped in this region.

So, the ruthenium complexes are better absorbers than the platinum complexes in the visual light region.

The absorption bands of these complexes in the 300-400 nm region were primarily assigned to the lowest π - π^* (**L1** or **L2**) transition because the band assignable to the lowest energy π - π^* (**L1** or **L2**) transition of free ligands was observed in the 300-370 nm region, as shown in Fig. 3. This π - π^* absorption band in both metal complexes was shifted to a long wavelength area compared with that of the free ligand upon coordination, and this phenomenon is supported by the simple coordination with two nitrogen atoms of the phenanthroline ring to the respective metal center discussed above. In addition, the lowest π - π^* (**L1**) absorption bands in the three present compounds are observed at somewhat long wavelength area relative to the π - π^* (**L2**) bands in the corresponding compounds. This might be attributable to the difference in symmetry between **L1** and **L2**, because the position of the nitrogen atom in the pyridyl ring differs between the two ligands and affects the molecular orbital energy levels of the extended π -conjugated **L1** and **L2** ligands.

The Ru(II) complexes show visible broad emission bands centered around 680 nm in deoxygenated acetonitrile at room temperature upon excitation at 425 nm, as shown in Fig. 4. These emissions were assigned to a typical triplet MLCT-based luminescence, which is well known in the emissions for ruthenium(II) polypyridine complexes. The quantum yield ($\phi_{\text{em}} = 0.107$) of the emission of **Ru1** is higher than that ($\phi_{\text{em}} = 0.073$) of **Ru2** and comparable to that ($\phi_{\text{em}} = 0.095$) of Ru(bpy)₃(PF₆)₂, which was measured as a standard sample for the quantum yield [19]. In spite of the emission observed in a long-wavelength area compared with a standard sample, the emission quantum yields of the present ruthenium complexes are relatively high, and these complexes are exactly phosphorescent dyes. Additionally, the excitation spectra of these compounds in the region between 300 nm and 500 nm were approximately compatible with the absorption spectra of these compounds in the same region. Also, the emission bands of Pt(II) complexes (Fig. 5) were observed in deoxygenated CH₂Cl₂ at room temperature upon the excitation at 425 nm, but the emission intensities of platinum compounds, **Pt1** and **Pt2**, were very weak. These emissions were assigned to a triplet MLCT as the main element, including the interligand transition (LLCT) as the minor element, according to a photophysical study that Chen's group conducted with similar platinum bipyridine compounds [23, 24]. The quantum yield ($\phi_{\text{em}} = 0.013$) of the emission of **Pt1** is higher

than that ($\phi_{\text{em}} = 0.008$) of **Pt2**, and this tendency is consistent with the luminescence of the corresponding ruthenium complexes. Additionally, the excitation spectra of these compounds in the region between 300 nm and 500 nm were compatible with the absorption spectra of these compounds in the same region. So, it was confirmed that these emissions could be derived from the present platinum complexes.

Conclusion

Ruthenium(II) polypyridyl and platinum(II) organometallic complexes were synthesized in moderate yields. In particular, platinum complexes were obtained from $\text{Pt}(\text{COD})(-\text{C}_6\text{H}_5\text{CH}_3)_2$ by the ligand exchange reaction because the dichloroplatinum complexes with the present phenanthroline ligands, $\text{Pt}(\text{L})\text{Cl}_2$ ($\text{L} = \text{L1}$ or L2), were hardly dissolved in the usual organic solvents.

Ruthenium complexes **Ru1** and **Ru2** showed the expected phosphorescence in CH_3CN , although platinum complexes **Pt1** and **Pt2** showed weak emissions compared to the ruthenium complexes. However, two types of these complexes have capabilities as metalloligands to other metal ions with two free pyridyl units. In addition, these two types of complexes could have different interactions with the other metal ions by their different charge potentials; ruthenium complexes have a 2+ cation unit, while platinum complexes are neutral compounds in solution.

We are currently extending our photophysical research for the selective detection of some metal ions with the present complexes and are constructing supramolecular macrocycles with other metal complex units.

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Table 1. Selected ^1H -NMR data of phenanthroline ligands and their complexes

Compound	Chemical shift (ppm)							
	phenH-2,9	phenH-4,7	phenH-5,6	pyH-2	pyH-3	pyH-4	pyH-5	pyH-6
L1	9.30	8.42	7.83	8.69		8.62	7.35	7.91
L2	9.30	8.44	7.83	8.68	7.48		7.48	8.68
Ru1	8.22	8.76	8.27	8.73		8.61	7.41	7.88
Ru2	8.25	8.79	8.28	8.64	7.43		7.43	8.64
Pt1	9.98	8.71	8.01	8.79		8.61	7.34	7.85
Pt2	9.85	8.65	7.98	8.62	7.35		7.35	8.62

The **L**, **Ru**, and **Pt** were measured in CDCl_3 , CH_3CN , and CD_2Cl_2 , respectively.

Figure Captions

Fig. 1 Molecular structures of present compounds **L**, **Ru**, and **Pt**.

Fig. 2 UV-Vis absorption spectra of ruthenium complexes **Ru1** (*solid line*) and **Ru2** (*dot line*) in CH₃CN at room temperature.

Fig. 3 UV-Vis absorption spectra of phenanthrolines, **L1** (*dot line*) and **L2** (*small dashed line*), and platinum complexes, **Pt1** (*solid line*) and **Pt2** (*large dashed line*), in CH₂Cl₂ at room temperature.

Fig. 4 Emission spectra of ruthenium complexes **Ru(bpy)₃(PF₆)₂** (*dot line*), **Ru1** (*solid line*), and **Ru2** (*small dashed line*) in CH₃CN at room temperature.

Fig. 5 Emission spectra of platinum complexes **Pt1** (*dot line*), and **Pt2** (*solid line*) in CH₂Cl₂ at room temperature.

Fig. 1

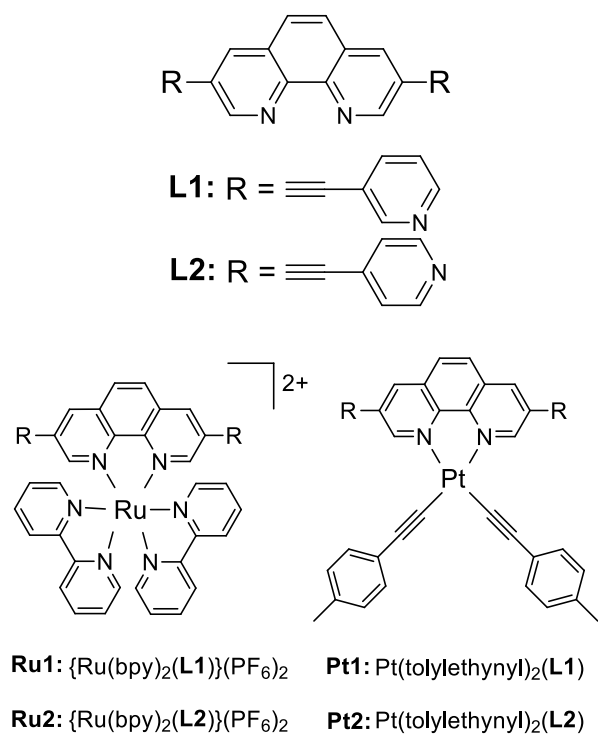


Fig. 2

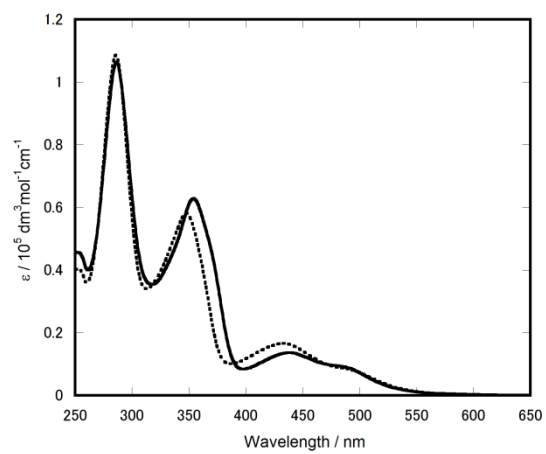


Fig. 3

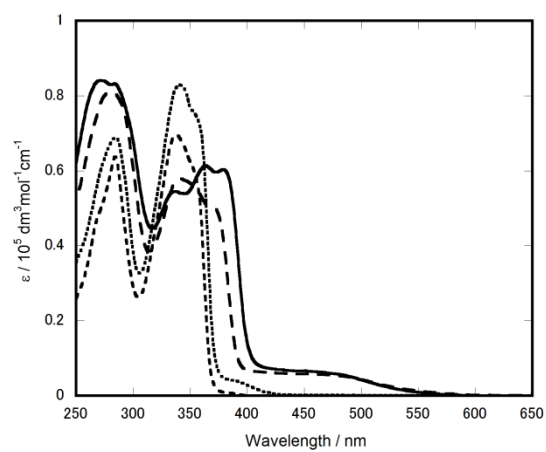


Fig. 4

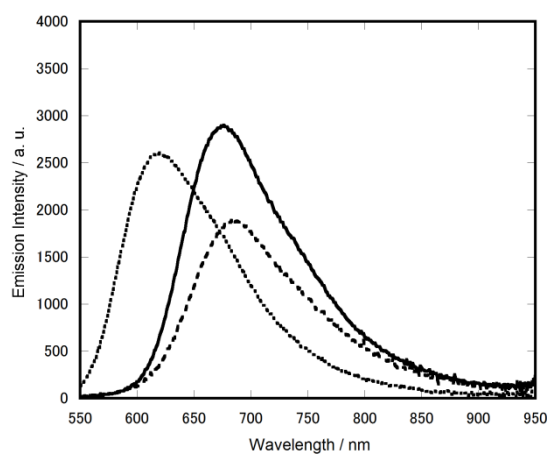


Fig. 5

