Preparation, Crystal Structures, Electrochemical and Spectroscopic Properties of Bis(2,2′-bipyridine)ruthenium(II) Complexes Containing 8-(Diphenylphosphino)quinoline or 2-(Diphenylphosphino)pyridine

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Mixed-ligand bis(2,2′-bipyridine)ruthenium(II) complexes containing a hybrid donor-type P–N ligand of 8-(diphenylphosphino)quinoline (Ph_2Pqn) or 2-(diphenylphosphino)pyridine (Ph_2Ppy), $[Ru(bpy)_2(Ph_2Pqn \text{ or } Ph_2Ppy)](PF_6)_2$ (**1** or **2**; bpy = 2,2′-bipyridine), have been prepared. The X-ray crystal structure analyses of **1** and **2** revealed that Ph_2Pqn and Ph_2Ppy act as a bidentate ligand to form a five- and four-membered chelate ring, respectively. The four-membered chelate ring formed by Ph_2Ppy has a very small bite angle (P(1)–Ru–N(1): 68.4(1)°), but the $Ru^{II}(bpy)_2$ moiety in **2** has a typically strain-free structure. On the other hand, in the Ph_2Pqn complex **1**, one of the bpy planes is skewed remarkably from the Ru coordination plane due to an intramolecular steric interaction with a phenyl ring of Ph_2Pqn. The redox potentials and the ^{1}MLCT transition energies of the Ph_2Pqn and Ph_2Ppy complexes (**1** and **2**) were not so different from the averaged values of those of the corresponding 1,2-bis(diphenylphosphino)benzene (dppb) and 1,10-phenanthroline (phen) complexes, $[Ru(bpy)_2(dppb \text{ or } phen)](PF_6)_2$ (**3** or **4**). These facts indicate that the electronic asymmetry inherently present in Ph_2Pqn and Ph_2Ppy does not affect remarkably the ground state properties of the complexes. However, unlike complexes **2**–**4**, the Ph_2Pqn complex **1** in EtOH/MeOH (4 : 1) glass at 77 K exhibited a novel dual emission, giving a biexponential emission decay. The shorter-lived (τ = 10.8 μs) emission is attributable to the bpy-based ^{3}MLCT emission, similar to the other Ru^{II}-polypyridine complexes, while the longer-lived (τ = 62.1 μs) emission can probably be assigned as arising from the quinoline-based $^3(\pi–\pi^*)$ excited state.

Ruthenium(II) polypyridine complexes have been studied extensively, owing to the potential applications of these complexes in diverse areas such as solar energy conversion, luminescent materials, and biotechnology.[1–4] A huge number of mixed-ligand ruthenium(II) polypyridine complexes have been synthesized for these purposes, and their electrochemical and spectroscopic properties as well as their photochemical reactivities have been investigated.[5–14] However, surprisingly few studies have been made so far for the mixed-ligand ruthenium(II) polypyridine complexes containing phosphines.[10–14] Complexes of *cis*-$[Ru(bpy)_2(P–P)]^{2+}$ (bpy = 2,2′-bipyridine, P–P = 1,2-bis(dimethyl- or diphenylphosphino)ethane (dmpe or dppe) or $(PPh_2Me)_2$) exhibit an appreciable emission at low temperature in rigid glass, but luminescence is virtually undetectable at room temperature in fluid solution due to the thermal activation from the emissive ^{3}MLCT to the non-radiative ^{3}d–d excited states.[13,14]

We are interested in the coordination chemistry of hybrid donor-type bidentate P–N ligands bearing phosphine and either pyridine,[16] quinoline[17] or amine groups.[18] Among such hybrid ligands, 8-(diphenylphosphino)quinoline (Ph_2Pqn) and 2-(diphenylphosphino)pyridine (Ph_2Ppy) are especially interesting for complexation with $Ru^{II}(bpy)_2$ center, because the diphenylphosphino donor group in these ligands is a weaker σ-donor[19] but a stronger π-acceptor than the quinolyl or pyridyl donor group. Therefore, the $Ru^{II}(bpy)_2$ complexes incorporating Ph_2Pqn or Ph_2Ppy may have characteristic ground state and/or excited state properties due to the electronic asymmetry[20] of the ligands. In this paper, we will report preparation and crystal structures of $[Ru(bpy)_2(Ph_2Pqn \text{ or } Ph_2Ppy)](PF_6)_2$ (**1** or **2**), and compare their electrochemical and spectroscopic properties with those of the related 1,2-bis(diphenylphosphino)benzene (dppb) and 1,10-phenanthroline (phen) complexes, $[Ru(bpy)_2(dppb \text{ or } phen)](PF_6)_2$ (**3** or **4**).

It was reported by Hudali et al. that a reaction of *cis*-$[RuCl_2(dmso)_4]$ with Ph_2Pqn did not afford any $Ru^{II}–Ph_2Pqn$ complex,[21] so that the complex **1** is the first example of a ruthenium(II) complex containing Ph_2Pqn. On the other hand, several $Ru^{II}–Ph_2Ppy$ complexes have been reported previously, these were utilized successfully as precursors for heterometallic dinuclear complexes bridged by Ph_2Ppy.[22–25] No mixed-ligand complexes with bpy have been synthesized so far, however.

Experimental

The phosphines, Ph_2Pqn[26] and Ph_2Ppy,[22] were prepared according to the literature methods, while dppb was purchased from Strem Co. Ltd. The complexes of *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$[27] and $[Ru(bpy)_2(phen)](PF_6)_2$ (**4**)[28] were prepared by the literature methods. All reactions were handled under an atmosphere of argon using standard Schlenk techniques until such time that air-stable ruthenium(II) phosphine complexes were formed.

Preparation of Complexes. A suspension of *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ (519 mg, 1.00 mmol) and Ph_2Pqn (313 mg, 1.00 mmol) in ethylene glycol (10 cm^3) was refluxed for 1 h to give a clear orange solution, and an excess amount of an aqueous NH_4PF_6 solution was added while hot. After the mixture was cooled to room temperature, the resulting orange precipitate was collected by filtration, washed with diethyl ether (30 cm^3), and dried in vacuo. The crude product was recrystallized from CH_2Cl_2/Et_2O or $CH_2Cl_2/MeOH$, affording orange crystals of $[Ru(bpy)_2(Ph_2Pqn)](PF_6)_2$ (**1**). Yield: 946 mg (93%). Anal. Found: C, 48.33; H, 3.01; N, 6.87%. Calcd for $C_{41}H_{32}F_{12}N_5P_3Ru$: C, 48.44; H, 3.17; N, 6.89%. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 58.81. The Ph_2Ppy and dppb complexes were prepared by a method similar to the above. Orange crystals of $[Ru(bpy)_2(Ph_2Ppy)](PF_6)_2$ (**2**): Yield: 61%. Anal. Found: C, 45.54; H, 3.09; N, 7.23%. Calcd for $C_{37}H_{30}F_{12}N_5P_3Ru$: C, 45.97; H, 3.13; N, 7.24%. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 43.86. Yellow microcrystals of $[Ru(bpy)_2(dppb)](PF_6)_2$ (**3**): Yield: 81%. Anal. Found: C, 52.03; H, 3.46; N, 4.83%. Calcd for $C_{59}H_{40}F_{12}N_4P_4Ru$: C, 52.23; H, 3.51; N, 4.87%. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 69.51.

Measurements. The $^{31}P\{^1H\}$ NMR spectra were recorded at 30 °C on a Jeol GSX-400 spectrometer using 85% H_3PO_4 as an external reference. UV-visible absorption spectra in CH_3CN were obtained on a Perkin-Elmer Lambda 19 spectrophotometer at room temperature. Cyclic voltammograms were measured at 25 °C on a BAS CV-27 voltammogram at a scan rate 200 mV s^{-1} in acetonitrile solutions ([complex] = 2.0×10^{-3} mol dm^{-3}; 0.1 mol dm^{-3} Bu_4NBF_4). A glassy carbon disk, a platinum wire, and a Ag/Ag^+ electrode (Ag/0.01 mol dm^{-3} $AgNO_3$) were used as the working, auxiliary, and reference electrodes, respectively. The redox potentials of samples were calibrated by the redox signal for the ferrocene/ferrocenium couple which was observed at +0.42 V vs Ag/Ag^+. Luminescence spectra in EtOH/MeOH (4 : 1) glass were recorded on a Shimadzu RF-5300PC spectrophotofluorometer at 77 K. Phosphorescence lifetimes were measured with a Hamamatsu C4780 system.

Crystallography. An orange prismatic crystal of **1** ($0.40 \times 0.24 \times 0.20$ mm) and an orange block crystal of **2** ($0.34 \times 0.22 \times 0.18$ mm) were each glued on the top of a glass fiber with epoxy resin and used for the X-ray diffraction study. The X-ray intensities ($2\theta_{max} = 60°$) were collected at 23 °C on an automated Rigaku AFC-5R four-circle diffractometer equipped with a graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Absorption corrections were applied by an empirical method based on three sets of Ψ-scan data.[29] The structures were solved by the direct method using SHELXS86 program[30] and refined on F^2 with all independent reflections by full-matrix least-squares methods using SHELXL97 program.[31] All non-hydrogen atoms were refined anisotropically, and H atoms were treated as riding models. All calculations were carried out using a TeXsan software package.[32] The crystallographic data are summarized in Table 1.

Table 1. Crystallographic Data for $[Ru(bpy)_2(Ph_2Pqn)](PF_6)_2$ (**1**) and $[Ru(bpy)_2(Ph_2Ppy)](PF_6)_2$ (**2**)

	1	**2**
Empirical formula	$C_{41}H_{32}F_{12}N_5P_3Ru$	$C_{37}H_{30}F_{12}N_5P_3Ru$
Fw	1016.70	966.64
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	*Pbca* (no. 61)
a / Å	12.638(3)	21.897(3)
b / Å	20.057(3)	25.961(4)
c / Å	16.801(2)	14.081(3)
β / deg	101.03(1)	90
V / Å^3	4180(1)	8005(2)
Z	4	8
D_{calc} / Mg m^{-3}	1.616	1.604
R_{int}	0.040	0.025
$F(000)$	2040	3872
μ(Mo $K\alpha$) / mm^{-1}	0.582	0.603
Refln/param ratio	11987/559	11676/550
$R1\{F^2: F^2 > 2\sigma(F^2)\}$	0.046	0.052
$wR2(F^2$: all data)	0.179	0.127
GOF	1.038	0.980

Tables of crystallographic data (excluding structure factors), atomic coordinates, thermal parameters, and full lists of bond lengths and angles are deposited as Document No. 75048 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers CCDC 188933 and 188934.

Results and Discussions

Preparation and Crystal Structures of $[Ru(bpy)_2(Ph_2Pqn$ or $Ph_2Ppy)](PF_6)_2$. The complex of $[Ru(bpy)_2(Ph_2Pqn, Ph_2Ppy$ or dppb$)](PF_6)_2$ was prepared in good yield by a reaction of *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ with either Ph_2Pqn, Ph_2Ppy or dppb in refluxing ethylene glycol,[7] followed by addition of an aqueous NH_4PF_6 solution. The products purified by repeated recrystallization gave satisfactory elemental analyses, and the $^{31}P\{^1H\}$ NMR spectrum of each complex showed a single resonance. The ^1H and $^{13}C\{^1H\}$ NMR also indicated that these complexes were not contaminated by impurities such as $[Ru(bpy)_3](PF_6)_2$ and unreacted *cis*-$[RuCl_2(bpy)_2]$.

The crystal structures of $[Ru(bpy)_2(Ph_2Pqn)](PF_6)_2$ (**1**) and $[Ru(bpy)_2(Ph_2Ppy)](PF_6)_2$ (**2**) were determined by the single-crystal X-ray diffraction method. The molecular structures of the complex cations in **1** and **2** are shown in Figs. 1 and 2, respectively. In the complexes, Ph_2Pqn and Ph_2Ppy act as a P–N type bidentate ligand to form a five- and four-membered chelate ring, respectively.

The Ph_2Ppy ligand has been utilized successfully to bridge homo- and heterodimetallic centers;[22–25] its chelate coordination mode to form a highly strained four-membered ring has also been reported.[23,24] The structure of the four-membered chelate ring formed by Ph_2Ppy in **2** is very similar to that in *cis*,*cis*-$[RuCl_2(CO)_2(Ph_2Ppy)]$;[23] the bite angle of P–Ru–N in the bis(2,2′-bipyridine) complex **2** is 68.4(1)° and that in the dichlorobis(carbonyl) complex is 68.7(2)°. The Ru–P(1) and Ru–N(1) bond lengths in **2** (2.304(2) and 2.092(4) Å, respectively) are slightly shorter than those in *cis*,*cis*-$[RuCl_2(CO)_2(Ph_2Ppy)]$ (Ru–P: 2.322(2), Ru–N: 2.119(6) Å); this difference is probably due to a difference in net charge on the Ru center. Owing to the highly strained four-membered chelate of Ph_2Ppy, the coordination geometry around the Ru center deviates remarkably from an ideal octahedron. It is obvious from the bond angles of P(1)–Ru–N(31): 164.9(1)° and N(1)–Ru–N(51): 171.9(2)° and shown in Fig. 3(b) that such a deviation is larger at the P(1)-donor site than the N(1)-donor

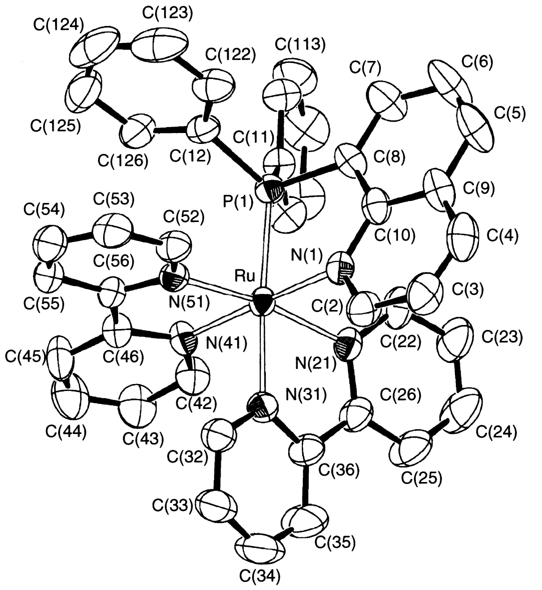

Fig. 1. Perspective drawing (50% probability level) of the cationic part of $[Ru(bpy)_2(Ph_2Pqn)](PF_6)_2$ (**1**). Selected bond lengths and angles: Ru–P(1) 2.282(1), Ru–N(1) 2.099(3), Ru–N(21) 2.097(3), Ru–N(31) 2.119(4), Ru–N(41) 2.070(3), Ru–N(51) 2.061(3) Å; P(1)–Ru–N(1) 82.5(1), N(21)–Ru–N(31) 77.6(1), N(41)–Ru–N(51) 78.2(1), P(1)–Ru–N(31) 176.2(1), N(1)–Ru–N(41) 176.9(1), N(21)–Ru–N(51) 170.8(1)°. Hydrogen atoms are omitted for clarity.

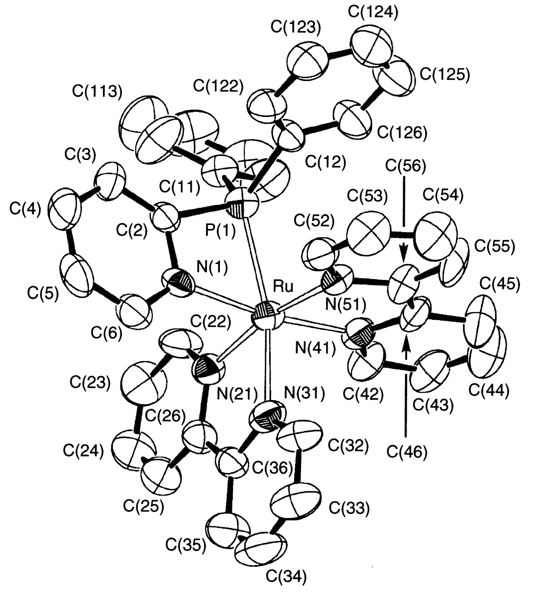

Fig. 2. Perspective drawing (40% probability level) of the cationic part of $[Ru(bpy)_2(Ph_2Ppy)](PF_6)_2$ (**2**). Selected bond lengths and angles: Ru–P(1) 2.304(2), Ru–N(1) 2.092(4), Ru–N(21) 2.082(5), Ru–N(31) 2.094(5), Ru–N(41) 2.042(4), Ru–N(51) 2.066(4) Å; P(1)–Ru–N(1) 68.4(1), N(21)–Ru–N(31) 77.6(2), N(41)–Ru–N(51) 78.6(2), P(1)–Ru–N(31) 164.9(1), N(1)–Ru–N(41) 171.9(2), N(21)–Ru–N(51) 169.3(2)°. Hydrogen atoms are omitted for clarity.

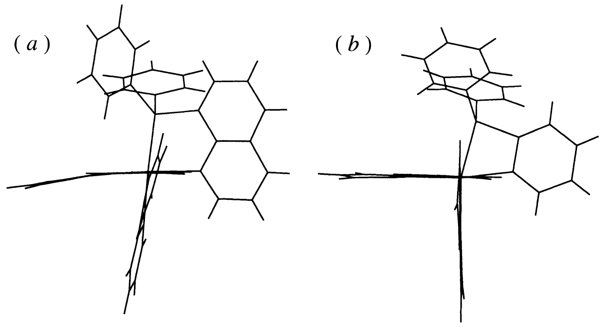

Fig. 3. Schematic drawings of the complex cations in (a) **1** and (b) **2**, viewed along the N(21)–Ru–N(41) axis.

site. This indicates a weaker *trans* influence of the Ph_2P-group in Ph_2Ppy than that in Ph_2Pqn due to the angular mismatch with the Ru^{II} d-orbitals. In fact, the elongation of the Ru–N(31) bond *trans* to Ru–P(1), as compared with the mutually *trans* Ru–N(bpy) bonds, is only 0.02 Å in **2**, while the corresponding elongation of the Ru–N(31) bond in **1** is twice as long, 0.04 Å.

The five-membered chelate ring formed by Ph_2Pqn in **1** has a bite angle of P(1)–Ru–N(1): 82.5(1)°, a typical value for the 8-quinolylphosphines found in their palladium(II) complexes;[17,33] the chelate ring is not planar, as indicated by the torsion angles of Ru–P(1)–C(8)–C(10): −12.0(4)° and Ru–N(1)–C(10)–C(8): 13.0(5)°. Although the octahedral arrangement of the donor atoms set around the Ru center in **1** was not distorted so much as that in the Ph_2Ppy complex **2** (see captions for Fig. 1), one of the bpy moieties in **1** was skewed remarkably from the Ru coordination plane, as illustrated in Fig. 3(a). Such a distortion of the bpy coordination geometry, as well as the non-planarity of the Ph_2Pqn chelate (Table 2), seem to be caused by the interligand steric congestion around the Ru center. The molecular modeling inspection for the ideally strain-free structure of $[Ru(bpy)_2(Ph_2Pqn)]^{2+}$ indicates that there are severe steric interactions between the phenyl groups of Ph_2Pqn and the bpy rings. Such steric congestion may be reduced in complex **2** because of the smaller bite angle of the four-membered

Table 2. Dihedral Angles between the Coordination Planes and the Quinolyl or Pyridyl Rings in Complexes **1** and **2**

Compound	1	2
plane{Ru,P(1),N(1)} vs plane qn(1)[a)]	16.14(8)	—
plane{Ru,P(1),N(1)} vs plane py(1)[b)]	—	3.9(2)
plane{Ru,N(21),N(31)} vs plane py(2)[c)]	11.0(1)	1.9(2)
plane{Ru,N(21),N(31)} vs plane py(3)[d)]	10.4(1)	1.2(2)
plane{Ru,N(41),N(51)} vs plane py(4)[e)]	6.7(1)	0.7(2)
plane{Ru,N(41),N(51)} vs plane py(5)[f)]	2.5(1)	1.5(2)
plane py(2)[c)] vs plane py(3)[d)]	12.3(2)	1.4(3)
plane py(4)[e)] vs plane py(5)[f)]	8.8(2)	1.8(2)

a) plane qn(1) defined by N(1) and C(2)–C(10). b) plane py(1) defined by N(1) and C(2)–C(6). c) plane py(2) defined by N(21) and C(22)–C(26). d) plane py(3) defined by N(31) and C(32)–C(36). e) plane py(4) defined by N(41) and C(42)–C(46). f) plane py(5) defined by N(51) and C(52)–C(56).

chelate ring formed by Ph_2Ppy.

Although the four-membered chelate ring formed by Ph_2Ppy in **2** was highly strained, the chelate coordination was found to be stable even in acetonitrile. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** in CD_3CN did not show any signal-broadening related to the dynamic equilibrium between the four-membered chelate and the unidentate P-donor coordination of Ph_2Ppy.[16] Furthermore, the NMR and UV-vis absorption spectra of **2** in acetonitrile(-d_3) were nearly identical with those in dichloromethane(-d_2); such results are indicative of an absence of any coordination of acetonitrile(-d_3) to the Ru^{II} center in the solution of **2**.

Electrochemistry and Absorption Spectroscopy. Table 3 lists the cyclic voltammetry and UV-vis absorption spectral data of a series of complexes, $[Ru(bpy)_2(Ph_2Pqn, Ph_2Ppy, dppb \text{ or } phen)](PF_6)_2$ (**1**–**4**). Each complex showed three reversible one-electron redox signals, which correspond to the $Ru^{III/II}$ oxidation process and the ligand-based $[Ru(bpy)_2(L)]^{2+/+}$ and $[Ru(bpy)_2(L)]^{+/0}$ reduction processes, as assigned for the other ruthenium(II) polypyridine complexes.[5]

For the first $[Ru(bpy)_2(L)]^{2+/+}$ and the second $[Ru(bpy)_2(L)]^{+/0}$ reduction potentials ($E_{1/2}(1)$ and $E_{1/2}(2)$, respectively) of the series of complexes **1**–**4**, it seems that there is no systematic change due to the incorporated ligands. The first reduction of the Ph_2Pqn complex **1** (-1.49 V vs SCE) appeared at a slightly less negative region than those of the phen complex **4** (-1.54 V) and $[Ru(bpy)_3](PF_6)_2$ (-1.55 V), as similarly observed for a series of analogous 8-(dimethylphosphino)quinoline (Me_2Pqn) complexes, $[Ru(bpy)_2(Me_2Pqn)](PF_6)_2$, C_1-$[Ru(bpy)(Me_2Pqn)_2](PF_6)_2$ and *fac*-$[Ru(Me_2Pqn)_3](PF_6)_2$, which exhibited the first reduction in a range of -1.47 to -1.48 V.[34] These observations indicate that the quinoline in 8-quinolylphosphines is more reductive than the bpy co-ligand. In other words, the π^* orbital of quinoline may be lower in energy than that of bpy in the mixed-ligand complex **1**.

The oxidation potential for the $Ru^{III/II}$ redox couple became more positive in the order of **4** (phen: $+1.08$ V) $<$ **1** (Ph_2Pqn: $+1.22$ V) $<$ **3** (dppb: $+1.49$ V). It has been reported that phosphines such as PPh_3 and PPh_2Me stabilize the Ru^{II} oxidation state more than 2,2′-bipyridine or 1,10-phenanthroline, owing to a better π-acceptability of the phosphines.[11,12] The observed difference in the oxidation potentials between complexes **1** and **3** (0.25 V) was remarkably larger than that between **1** and **4** (0.14 V). This is also indicative of the π-acceptability of $(dppb)_{1/2}$ (or $Ph_2PC_6H_4$-) group being stronger than that of $(phen)_{1/2}$ (or quinolyl) group, because the HOMO of complex **3** should be stabilized by a π-back bonding with a d orbital of the P donor atom of Ph_2P- group, while the HOMO of complex **1** or **4** does not have such a π-back bonding. The $Ru^{III/II}$ oxidation of the Ph_2Ppy complex **2** took place at almost identical potential for the Ph_2Pqn complex **1**, although the four-membered chelate coordination of Ph_2Ppy gave a large deviation for the Ph_2P- donor site from the ideally octahedral coordination geometry around the Ru^{II} center, and therefore, the π-back bonding between Ru^{II} and Ph_2P- donor in the Ph_2Ppy complex **2** seemed to become less effective than that in the Ph_2Pqn complex **1**. However, if the Ph_2P- donor has a better π-acceptability than bpy, the HOMO of the two complexes would be roughly the same in energy, independent of the π-stabilization energy. Therefore, these oxidation potentials of a series of complexes indicate that the diphenylphosphino donor group in Ph_2Pqn, Ph_2Ppy and dppb is, in fact, a better π-acceptor than 2,2′-bipyridine or quinoline.

Figure 4 shows UV-visible absorption spectra of complexes **1**–**4**. Each complex showed two intense absorption envelopes, in the regions of 20000–30000 cm^{-1} and 30000–37000 cm^{-1}. The phen complex **4** gave an absorption band at 22300 cm^{-1} accompanied with a vibrational structure at the higher energy side; this absorption envelope has been assigned as the MLCT transition band.[35] The corresponding absorption envelopes of the Ph_2Pqn, Ph_2Ppy and dppb complexes **1**–**3** were rather broad without showing explicit vibrational structures, and their intensity became almost a half of that of complex **4**. The observed difference in the MLCT transition energies between complexes **1** and **4** is 1600 cm^{-1}, and the difference between complexes **1** and **3** is 2600 cm^{-1}. These values are consistent with the differences in the $Ru^{III/II}$ oxidation potentials: 0.14 V (1100 cm^{-1}) and 0.27 V (2200 cm^{-1}).

The higher energy absorption band of the phen complex **4** at 35100 cm^{-1} can be assigned as the bpy-based intraligand π–π^* transition (the phen-based intraligand π–π^* transition was observed at 37900 cm^{-1}). The Ph_2Pqn and Ph_2Ppy complexes **1** and **2** showed the bpy-based intraligand π–π^* transition band at the same position as complex **4**, but this band was accompanied by a broad shoulder at the lower energy side. This absorption shoulder is probably due to the quinoline-based or the pyridine-based intraligand π–π^* transition. The higher energy absorption envelope of the dppb complex observed at 30000–

Table 3. Cyclic Voltammetry ($E_{1/2}$/V vs SCE)[a] and UV-Visible Absorption [σ_{max} / 10^3 cm^{-1} (ε_{max}/10^3 dm^3 mol^{-1} cm^{-1})][b] Data of the Complexes $[Ru(bpy)_2(L)](PF_6)_2$

Complex	L	Oxidation	Reduction		$\Delta E_{1/2}$[c]	Absorption	
		$E_{1/2}(Ru^{III/II})$	$E_{1/2}(1)$	$E_{1/2}(2)$		MLCT	π–π^*
1	Ph_2Pqn	$+1.22$	-1.49	-1.72	21.9	23.9 (10.02)	35.1 (46.98)
2	Ph_2Ppy	$+1.25$	-1.52	-1.72	22.3	24.4 (9.26)	35.2 (46.91)
3	dppb	$+1.49$	-1.51	-1.76	24.2	26.5 (8.09)	31.3,[d] 36.0 (34.92)
4	phen	$+1.08$	-1.54	-1.71	21.1	22.3 (19.04), 23.6,[d] 25.9[d]	35.1 (75.96), 37.9 (67.31)

a) In CH_3CN at 25 °C, all redox processes are reversible. b) In CH_3CN at room temperature. c) $\Delta E_{1/2} = E_{1/2}(Ru^{III/II}) - E_{1/2}(1)$ in 10^3 cm^{-1} (1 eV = 8066 cm^{-1}). d) Shoulder.

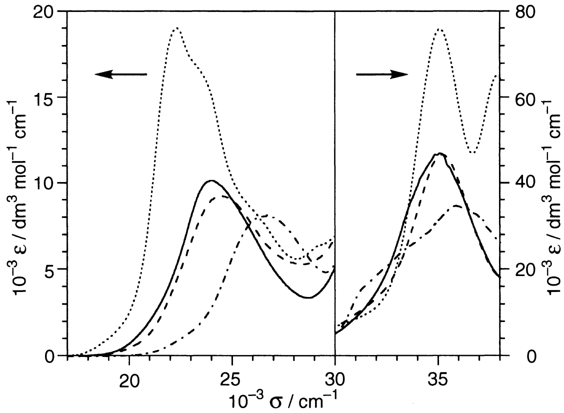

Fig. 4. UV-vis absorption spectra of complexes **1**–**4** in acetonitrile at room temperature. (———) complex **1**, (– – – –) complex **2**, (– · – · –) complex **3** and (- - - - - -) complex **4**.

37000 cm^{-1} seems to be composed of at least three bands, which probably originate from the intraligand π–π* transitions of phenylene, phenyl and 2,2′-bipyridine moieties.

Luminescence Spectra. Complexes **1**–**3** in acetonitrile at room temperature did not show a measurable luminescence, but an intense orange or red luminescence was observed in EtOH/MeOH (4:1) glass at 77 K (Fig. 5), similarly to the other Ru^{II} complexes containing phosphines.[13,14] The phen complex **4** exhibited an emission manifold of the highest energy maximum at 573 nm with a pronounced vibrational progression of $\Delta\nu = 1230$ cm^{-1}, and the emission lifetime at 77 K in EtOH/MeOH glass was determined as 5.6 μs (Table 4). This emission has been assigned as arising from the ^{3}MLCT excited state.[35]

It has been demonstrated that, when phosphines coordinate to a Ru^{II}–polypyridine center, the ^{3}MLCT emission band is blue-shifted with a smaller vibrational progression and the emission lifetime becomes slightly longer.[13,14] The dppb complex **3** showed such a luminescence behavior; the emission maximum was observed at 514 nm with vibrational progression of $\Delta\nu = 920$ cm^{-1} and the emission lifetime was 12.4 μs; these values are similar to those reported for the analogous 1,2-bis(diphenylphosphino)ethane (dppe) complex, $[Ru(bpy)_2(dppe)](PF_6)_2$[14] (our measurement for this dppe complex gave $\lambda_{max}^{em} = 518$ nm, $\Delta\nu = 990$ cm^{-1} and $\tau = 14.0$ μs).

Table 4. Luminescence Spectroscopic Data[a)] (λ_{max}^{em}/nm, τ / μs) of the Complexes $[Ru(bpy)_2(L)](PF_6)_2$

Complex	L	λ_{max}^{em}	τ
1	Ph_2Pqn	557, 589, 633[b)]	10.8, 62.1
2	Ph_2Ppy	551, 583, 631[b)]	5.3
3	dppb	514, 540, 571[b)]	12.4
4	phen	573, 617, 681[b)]	5.6

a) In EtOH/MeOH (4:1) glass at 77 K. b) Broad shoulder whose maximum position was estimated by the curve-fitting analysis.

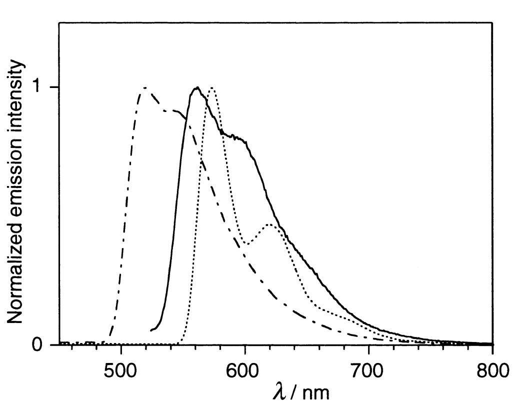

Fig. 5. Normallized emission spectra of complexes **1** (———), **3** (– · – · –) and **4** (- - - - - -) in EtOH/MeOH (4:1) glass at 77 K. Excitation wavelength is 285 nm for complexes **1** and **3** and 265 nm for complex **4**. The emission spectra were found to be independent of the excitation wavelength; i.e. the excitation with the light corresponding to the ^{1}MLCT transition gave the same emission spectrum.

The Ph_2Pqn complex **1** gave an intense emission of the highest energy maximum at 557 nm with a longer wavelength shoulder at 589 nm (vibrational progression, $\Delta\nu = 970$ cm^{-1}). The emission spectrum was independent of the excitation wavelength, and the excitation spectra of complex **1** monitored by the emission at 562 and 600 nm were found to match the absorption spectrum. The most characteristic feature of the emission of complex **1** was found in the analysis of the emission lifetime. As shown in Fig. 6, monitoring the emission decay of complex **1** at 562 nm at 77 K yielded a biexponential kinetic trace that can be fitted to lifetimes of 10.8 and 62.1 μs. In cases where such a dual emission is observed, the contamination from impurities is always a concern. However, we believe that the dual emission is inherently present in the Ph_2Pqn complex **1**, since the sample is pure enough to give satisfactory elemental analyses and NMR spectra, and since a similar dual emission has also been observed for $[Ru(bpy\ or\ phen)_2(Me_2Pqn)](PF_6)_2$ and C_1-$[Ru(bpy)(Me_2Pqn)_2](PF_6)_2$.[34] The shorter-lived emission can be assigned as arising from the ^{3}MLCT excited state, because the lifetime ($\tau = 10.8$ μs) is in between the lifetimes of the corresponding phen and dppb complexes **4** and **3**. The longer-lived component results probably from the quinoline-based ^{3}(π–π*) emissive excited state,

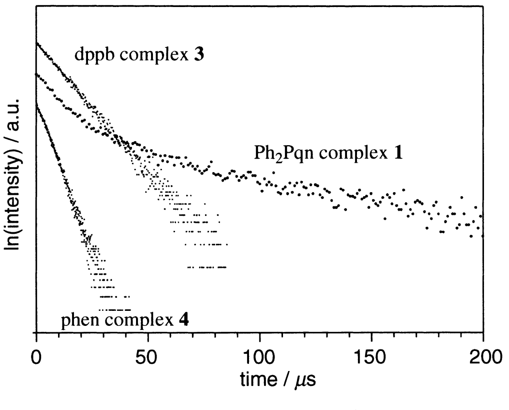

Fig. 6. Emission decay of complexes **1** (at 562 nm), **3** (at 540 nm) and **4** (at 573 nm) in EtOH/MeOH (4:1) glass at 77 K following pulsed excitation ($\lambda_{ex} = 337$ nm).

because *fac*-$[Ru(Me_2Pqn)_3](PF_6)_2$ showed a very long-lived (τ = 920 μs) emission (with the maximum at 536 nm) from the quinoline-based $^3(\pi\text{–}\pi^*)$ excited state.[34]

The Ph_2Ppy complex **2** gave a similar emission spectrum, the highest energy maximum being observed at 551 nm, to the Ph_2Pqn complex **1**. However, the kinetics fit a normal single-exponential decay with a lifetime of 5.3 μs. The non-existence of dual emission for the Ph_2Ppy complex also suggests that the longer-lived emission of the Ph_2Pqn complex **1** originates from the quinoline-based $^3(\pi\text{–}\pi^*)$ emission.

Concluding Remarks

In this study, mixed-ligand bis(2,2′-bipyridine)ruthenium(II) complexes with hybrid donor-type P–N ligands of Ph_2Pqn and Ph_2Ppy, $[Ru(bpy)_2(Ph_2Pqn \text{ and } Ph_2Ppy)](PF_6)_2$, were prepared and characterized. These complexes are stable in the solid states and in solution, but have rather large steric strains as compared with those for $[Ru(bpy)_3](PF_6)_2$.[15] Owing to the intramolecular steric congestion between the phenyl group of Ph_2Pqn and the 6-positioned H atom of pyridine group of bpy, one of the bpy ligands in the Ph_2Pqn complex is skewed largely from the Ru coordination plane. On the other hand, because of a very small bite angle of the four-membered chelate ring formed by Ph_2Ppy, the ideally octahedral coordination structure around the Ru^{II} center showed a large deviation, particularly for the Ph_2P- donor site. Such a deviation weakens the strengths of the *trans* influence, and probably the π-acceptability, of the Ph_2P- group of Ph_2Ppy so these values become lower than those of the Ph_2P- group of Ph_2Pqn.

The electrochemical and absorption spectral studies suggested that the electronic asymmetry inherently present in Ph_2Pqn and Ph_2Ppy does not affect remarkably the ground state properties of their Ru^{II} complexes, which can be presumed to be similar to those of the analogous phen and dppb complexes. Also, the emission spectra of the Ph_2Pqn and Ph_2Ppy complexes were similar to those of the phen and dppb complexes, with the maximum emission energy in the order of phen $<$ Ph_2Ppy $<$ Ph_2Pqn $<$ dppb. However, the Ph_2Pqn complex exhibited an unusual dual emission, arising from the bpy-based ^{3}MLCT and the quinoline-based $^3(\pi\text{–}\pi^*)$ emissive excited states. For ruthenium(II) polypyridine complexes, such a dual emission has been rarely observed in a glass matrix; there have been three kinds of examples reported previously. In 1987, Blakley and DeArmond observed firstly a dual emission for $[Ru(\text{bpy or phen})(Hdpa)_2]^{2+}$ (Hdpa = 2,2′-dipyridylamine), which originated from the ^{3}MLCT and the interligand charge-transfer $^3(n_{\text{Hdpa}}\text{–}\pi^*_{(\text{bpy or phen})})$ emissive excited states.[8] Recently, Vos et al. have accounted for a dual emission from $[Ru(bpy)_2(pztr)]^+$ (pztr = 3-(pyradin-2-yl)-1,2,4-triazolate) by the presence of two weakly coupled emitting states: the bpy-based ^{3}MLCT and the pyrazine-based ^{3}MLCT excited states.[9] Other examples of the Ru^{II} complexes exhibiting a dual emission are the $[Ru(bpy)_3]^{2+}$-type complexes with a phosphorescent pendant group such as arenes,[4] which have received great interest during these years because of the relation to the artificial photosynthesis system. In the complexes, the two components contributing to the dual emission are the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ moiety and the $^3(\pi\text{–}\pi^*)$ state of the arene substituent(s), which are nearly isoenergetic and are not in equilibrium. The observed dual emission for the present complex **1** is thus caused by a different mechanism from those of the above-mentioned complexes; the quinoline-based $^3(\pi\text{–}\pi^*)$ emissive excited states of 8-quinolylphosphines play an important role. This may offer a new approach to the use of ruthenium(II) 8-quinolylphosphine complexes as artificial photosynthetic catalysts.

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