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Synthesis and Protonation-deprotonation Reactions of Ruthenium(II) Complexes Containing 2,2′-Bibenzimidazole and Related Ligands

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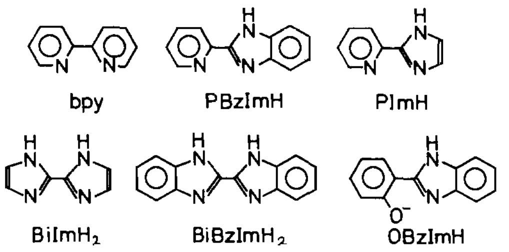
New ruthenium(II) complexes, $[Ru(bpy)_2L]^{n+}$ (bpy = 2,2′-bipyridine; n = 1, L = 2-(o-hydroxyphenyl)benzimidazole(OBzImH); n = 2, L = 2-(2-pyridyl)benzimidazole(PBzImH), 2-(2-pyridyl)imidazole(PImH), and 2,2′-bibenzimidazole($BiBzImH_2$)), have been prepared. From the spectral and electrochemical measurements the metal-to-ligand charge transfer bands and oxidation potentials are rationalized in terms of the donor property of L, which increases in the order of bpy < PBzImH < PImH < $BiBzImH_2$ < 2,2′-biimidazole($BiImH_2$) < OBzImH. Acid ionization constants of the coordinated ligands have been measured, and some of the deprotonated complexes have been isolated. The deprotonated forms of ligands are suggested to have a stronger π-donor property than the protonated forms. The emissions in the 600–670 nm region were observed for the $[Ru(bpy)_2L]^{2+}$ complexes (L = PBzImH, PImH, $BiBzImH_2$, and $BiImH_2$), both at room temperature and at 77 K. The emission lifetime decreases with increasing the number of imidazole group in the ligand L. The N–H bond of the imidazole group is suggested to provide a rapid deactivation pathway on the excited state.

Introduction

The coordination of imidazole and its derivatives to transition metal ions has attracted much attentions since the imidazole ring of histidine plays an important role in the metalloproteins [1]. In several heme proteins such as myoglobin and cytochrome c, pyrole hydrogen bonding or hydrogen ionization on imidazole coordinated to the metal ions is known to control structure and reactivity [2]. Recently, the existence of the imidazolate-bridged copper(II)–zinc(II) active site has been elucidated by X-ray crystallography, and the protonation-deprotonation reactions of imidazole moiety after the Cu–Zn bridging splitting was suggested to be responsible for the dismutase activity [3].



Scheme 1. Structure of the ligands and their abbreviations.

On the other hand, considerable evidence on the redox and photochemical properties of bis(2,2′-bipyridine)ruthenium(II) complexes have been accumulated [4], but few mixed-ligand ruthenium(II) complexes containing both 2,2′-bipyridine and imidazole derivatives have been reported so far [5]. In previous letters dealing with the synthesis and properties of new ruthenium complexes containing 2-(2-pyridyl)benzimidazole(PBzImH) and 2,2′-bibenzimidazole($BiBzImH_2$), we found that the deprotonation of coordinated imidazoles not only alters the oxidation potentials of the Ru(II) complexes but also manifests the bridging nature of the ligand between the two $Ru(diimine)_2$ moieties (diimine = 2,2′-bipyridine(bpy) or 1,10-phenanthroline(phen)) [6]. The author wishes to report here that ruthenium complexes containing imidazole or benzimidazole derivatives can tune the redox potentials or emission properties by the deprotonation.

Experimental

Materials

Ruthenium trichloride and bpy were of reagent grade and used as supplied. $Ru(bpy)_2Cl_2$ [7], PBzImH [8], 2-(2-pyridyl)imidazole(PImH) [9], 2-(*o*-

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hydroxyphenyl)benzimidazole(OBzImH) [10], BiBzImH$_2$ [11] and 2,2′-biimidazole(BiImH$_2$) [12] were prepared as described in the literatures. Tetrabutylammonium perchlorate (TBAP) was synthesized by the literature method [13], recrystallized from ethanol, and vacuum-dried. Acetonitrile was dried over phosphorus pentoxide for spectral measurements and further dried over calcium hydride before use for electrochemical measurements. Doubly-distilled water was also used as a solvent in spectroscopic measurements.

Synthesis of Complexes

[Ru(bpy)$_2$L](ClO$_4$)$_2$ (L = PBzImH, PImH, BiImH$_2$, and BiBzImH$_2$)

A suspension of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O (1 g, 2.1 mmol) in ethanol/water (1:1 v/v, 80 cm^3) was refluxed under nitrogen until dissolution was complete (*ca.* 1.5 h). To the resulting solution was added PBzImH (0.48 g, 2.4 mmol) and the mixture refluxed for further 3 h, during which time the color changed from brown to red. The red solution was evaporated under reduced pressure to remove ethanol and filtered. To the filtrate was added sodium perchlorate (1 g, 7.1 mmol) to yield a reddish-orange precipitate of [Ru(bpy)$_2$(PBzImH)](ClO$_4$)$_2$, which was collected by filtration and recrystallized from methanol, 84% yield. *Anal.* Calcd for $C_{32}H_{25}N_7Cl_2O_8Ru$: C, 47.59; H, 3.13; N, 12.14%. Found: C, 47.42; H, 3.14; N, 11.84%. Λ_M = 343 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} mol dm^{-3} in CH$_3$CN).

The PImH, BiImH$_2$, and BiBzImH$_2$ complexes were similarly prepared by the reaction of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O with the appropriate ligand, 70, 75 and 60% yield, respectively. L = PImH: *Anal.* Calcd for $C_{28}H_{23}N_7Cl_2O_8Ru$: C, 44.39; H, 3.07; N, 12.95%. Found: C, 44.40; H, 2.97; N, 13.04%. Λ_M = 318 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} mol dm^{-3} in CH$_3$CN). L = BiImH$_2$: *Anal.* Calcd for $C_{26}H_{24}N_8Cl_2O_9Ru$: C, 40.85; H, 3.17; N, 14.66%. Found: C, 40.60; H, 2.84; N, 14.59%. Λ_M = 310 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} mol dm^{-3} in CH$_3$CN). L = BiBzImH$_2$: *Anal.* Calcd for $C_{34}H_{30}N_8Cl_2O_{10}Ru$: C, 46.26; H, 3.43; N, 12.70%. Found: C, 46.12; H, 2.99; N, 12.82%. Λ_M = 339 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} mol dm^{-3} in CH$_3$CN).

[Ru(bpy)$_2$(OBzImH)](ClO$_4$)

A suspension of Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.4 g, 0.8 mmol) in an ethanol/water solution (1:1 v/v, 50 cm^3) was heated for 1 h to give a transparent solution, to which was added OBzImH (0.21 g, 1 mmol) and calcium carbonate (0.1 g, 1 mmol). After being heated for further 3 h, the solution was concentrated to about a half volume under reduced pressure and filtered. Sodium perchlorate (0.3 g, 2.1 mmol) was added to the filtrate to give black microcrystals, which were collected by filtration and recrystallized from methanol, 84% yield. *Anal.* Calcd for $C_{33}H_{25}N_6ClO_5Ru$: C, 54.89; H, 3.50; N, 11.64%. Found: C, 54.48; H, 3.65; N, 11.41%. Λ_M = 153 Ω^{-1} cm^2 mol^{-1} (4.0 × 10^{-4} mol dm^{-3} in CH$_3$CN).

[Ru(bpy)$_2$(PBzImH)](ClO$_4$)·H$_2$O

A methanol (30 cm^3) solution of [Ru(bpy)$_2$(PBzImH)](ClO$_4$)$_2$ (0.3 g, 0.4 mmol) was added to a sodium methoxide obtained *in situ* by the dissolution of sodium (0.04 g, 1.7 mmol) in methanol (40 cm^3); the color of the solution changed from reddish orange to brown immediately. After being heated for about 1.5 h, the solution was concentrated to half volume *in vacuo.* The resulting solution was allowed to stand at room temperature to give a precipitate, which was collected and recrystallized from methanol, 96% yield. *Anal.* Calcd for $C_{32}H_{26}N_7ClO_4Ru$: C, 53.00; H, 3.62; N, 13.53%. Found: C, 52.88; H, 3.16; N, 13.63%. Λ_M = 150 Ω^{-1} cm^2 mol^{-1} (2.0 × 10^{-4} mol dm^{-3} in CH$_3$CN).

[Ru(bpy)$_2$(BiBzIm)]·2H$_2$O

This complex was prepared by a procedure similar to that described above, using [Ru(bpy)$_2$(BiBzImH$_2$)](ClO$_4$)$_2$ in place of [Ru(bpy)$_2$(PBzImH)](ClO$_4$)$_2$, 80% yield. *Anal.* Calcd for $C_{34}H_{28}N_8O_2Ru$: C, 59.90; H, 4.15; N, 16.44%. Found: C, 59.93; H, 4.28; N, 16.03%. Λ_M = 2.0 Ω^{-1} cm^2 mol^{-1} (1.0 × 10^{-4} mol dm^{-3} in CH$_2$Cl$_2$).

Physical Measurements

Electric conductivities were measured for CH$_3$CN or CH$_2$Cl$_2$ solutions of the Ru complexes ((1.0–5.0) × 10^{-4} mol dm^{-3}) by using a Yokogawa F-255A Universal Bridge. Electronic spectra were recorded on a Shimadzu UV-210A double-beam spectrophotometer equipped with a 1 cm quartz cell. The measurements of pH were made with a TOA HM-5B pH meter standardized with pH buffers at pH 4.0 and 9.0. The spectrophotometric titrations were performed with 1.0 × 10^{-4} mol dm^{-3} solutions of the complex dissolved in 5% methanol/95% water, except for [Ru(bpy)$_2$(BiBzImH$_2$)](ClO$_4$)$_2$ where a mixture of 50% methanol/50% water was used as a solvent for complete dissolution of the fully deprotonated complex. The solution was titrated with a 0.01 mol dm^{-3} NaOH or HCl aqueous solution.

Cyclic voltammetry was measured for degassed acetonitrile solutions containing ruthenium complexes (1.0 × (10^{-3}–10^{-4}) mol dm^{-3}) and TBAP (0.1 mol dm^{-3}) as a supporting electrolyte by using a Hokuto Denko HA-301 or HA-104 potentiostat-galvanostat, a Nikko Keisoku NPS-2 potential sweeper or a Hokuto Denko HF-201 function generator, and a Riken Denshi F-3DP x–y recorder. The working electrode and the auxiliary electrode were respectively a Beckman stationary platinum

TABLE I. Electronic Spectral Data for $[Ru(bpy)_2L](ClO_4)_n$ Complexes in Acetonitrile.

L	Protonated Form		Deprotonated Form[a]	
	n	λ_{max}, nm (logε)	n	λ_{max}, nm (logε)
PBzImH	2	458(4.11), 317(4.41), 289(4.78) 244(4.50)	1	493(3.98), 328(4.36), 293(4.78), 246(4.59)
PImH	2	460(4.02), 426(4.00), 388sh 355sh, 289(4.85), 244(4.35)	1	500(3.96), 446sh, 377sh 330sh, 293(4.76), 245(4.33)
$BiBzImH_2$	2	463(4.07), 350(4.64), 332(4.57), 320sh, 291(4.79), 243(4.58)	1	507(3.96), 341(4.53), 327(4.49), 294(4.77), 243(4.64)
			0	551(3.96), 334(4.48), 298(4.74), 245(4.79)
$BiImH_2$	2	473(3.97), 340(4.03), 289(4.78), 242(4.37)	1	513(3.98), 334(4.00), 292(4.73), 244(4.40)
			0	562(3.93), 360(3.92), 294(4.69), 244(4.49)
OBzImH	1	530(3.85), 376(4.10), 322(4.12), 299(4.71), 244(4.60)	0	583(3.84), 382(4.22), 298(4.71), 240(4.71)

[a]Formed *in situ* by adding $(C_4H_9)_4NOH$.

disk (4 mm diameter) and a 4 cm^2 platinum plate. The reference electrode, separated from the voltammetric cell by a salt bridge, was $Ag/AgNO_3$ (0.01 mol dm^{-3} in CH_3CN). The silver quasireference electrode was calibrated during each experiment relative to the ferrocene/ferrocium couple ($E_{1/2}$ = +0.310 V *vs.* SCE in CH_3CN [14]).

All emission spectra at room temperature and 77 K were measured with a Hitachi MPF-4 fluorescence spectrophotometer. Emission spectra were uncorrected. The solutions for emission measurements were degassed by freeze-pump-thaw cycles three times and sealed under vacuum. Lifetime measurements were obtained using a home-made nitrogen laser as a pulsed light source (pulse width 10 ns). The emission titrations were done in the similar conditions to spectrophotometric titrations, except for measuring the solution saturated with nitrogen gas.

Results and Discussion

Preparation of Complexes

The reaction of dichlorobis(2,2′-bipyridine)ruthenium(II) with the appropriate ligands in ethanol/water (1:1 v/v) gave the desired mixed-ligand complexes as perchlorates, of which $[Ru(bpy)_2(BiImH_2)](PF_6)_2$ has been reported during the course of this study [5]. These new complexes are soluble in acetone and acetonitrile, and relatively soluble in ethanol, methanol, and water. The molar conductivities at the concentration of 1.0×10^{-4} mol dm^{-3} in acetonitrile are 310 ~ 350 Ω^{-1} cm^2 mol^{-1} for PBzImH, PImH, $BiImH_2$, and $BiBzImH_2$ complexes, and 153 Ω^{-1} cm^2 mol^{-1} for OBzImH complex, respectively. These results are consistent with the 2:1 electrolytes for the PBzImH, PImH, $BiImH_2$, and $BiBzImH_2$ complexes and the 1:1 electrolyte for the OBzImH complex. Although all the complexes obtained here reacted with sodium methoxide, only the reaction products with the PBzImH and $BiBzImH_2$ complexes have been isolated as a pure solid. Conductivity measurements indicate that the deprotonated PBzIm complex is a 1:1 electrolyte, and the BiBzIm complex a non-electrolyte. The deprotonated PBzIm and BiBzIm complexes reacted with $HClO_4$ to regenerate the PBzImH and $BiBzImH_2$ complexes quantitatively. The reversibility of this protonation-deprotonation reactions is confirmed from the pH dependence on the absorption spectra of aqueous solutions of not only PBzImH and $BiBzImH_2$ complexes but the other complexes obtained here.

Absorption Spectra

Absorption spectra for the complexes obtained here in acetonitrile are given in Table I. The low energy absorption bands at 460 ~ 530 nm may be assigned to metal-to-ligand charge transfer (MLCT) transitions and two bands with the maxima at 290 nm and 240 nm to bipyridine intraligand π–π^* transitions by referring spectra of $[Ru(bpy)_3]^{2+}$ and a number of $[Ru(bpy)_2L_2]^{2+}$ [15]. The MLCT transition energies of $[Ru(bpy)_2L](ClO_4)_n$ (n = 1 or 2) decrease in the order of L = bpy > PBzImH > PImH > $BiBzImH_2$ > $BiImH_2$ > OBzImH, which is consistent with the π-donor ability of the imidazole ligands; a stronger π-donor ligand increases electron density on the metal to result in the decrease of the MLCT band energies. Thus, the π-donor strength of

TABLE II. Acid Ionization Constants of $[Ru(bpy)_2L](ClO_4)_n$ at 25 °C.[a]

n	L	pK_{a1}	pK_{a2}
2	PBzImH	6.8 ± 0.1	
2	PImH	7.9 ± 0.1	
2	$BiBzImH_2$[b]	5.7 ± 0.1	10.1 ± 0.2
2	$BiImH_2$	7.3 ± 0.1	~12
1	OBzImH	11.0 ± 0.2	

[a]In 5% methanol/95% water. [b]In 50% methanol/50% water.

TABLE III. Cyclic Voltammetric Data for the Protonated $[Ru(bpy)_2L](ClO_4)_n$ Complexes.[a]

n	L	$E_{1/2}$[b], V *vs.* SCE	
		Oxidation	Reductions
2	PBzImH	+1.17(70)	−1.49(60), −1.76(60)
2	PImH	+1.14(70)	−1.52(70), −1.78(80)
2	$BiBzImH_2$	+1.12(70)	−1.60(80), −1.90(80)
2	$BiImH_2$	+1.04(80)	−1.66(70), −1.96(60)
1	OBzImH	+0.39(80)	−1.67(70), −2.00(80)

[a]Measured in acetonitrile containing 0.1 mol dm^{-3} TBAP as a supporting electrolyte at a platinum electrode. [b]$E_{1/2}$ values are the average of the anodic and cathodic peak potentials. The values in parentheses are the separation of anodic and cathodic peak potentials.

substituents in these ligands increases in the order of pyridine < benzimidazole < imidazole ≅ phenoxide.

The absorption spectra of $[Ru(bpy)_2(PImH)](ClO_4)_2$ in 5% methanol/95% water at various pH is depicted in Fig. 1, which shows two isosbestic points at 393 and 474 nm. This is indicative of the presence of the acid-base equilibrium in this system. Similar lower energy shifts of the absorption maxima on deprotonation of the coordinated imidazole ligands were observed for PBzImH, $BiBzImH_2$, $BiImH_2$, and OBzImH complexes. The acid ionization constants pK_{a1} and/or pK_{a2} calculated from the spectra at various pH are collected in Table II.

Comparison of the pK_a values of the PImH and PBzImH complexes (Table II) with those of free PImH and PBzImH (13.4 and >12 respectively [16]) indicates that the acidity of these ligands increases upon their coordination to the ruthenium ion. This is consistent with the ease of deprotonation of the coordinating ligands. The pK_a values of complexes of the benzimidazole derivatives are smaller than those of the imidazole derivatives (Table II). This is due to the electronwithdrawing effect of benzene ring in benzimidazole. Recently, the acid ionization constants in a series of $[Mo(\eta\text{-}C_5H_5)_2(L)]^{2+}$ (L = PBzImH, PImH, OBzImH *etc.*) have been reported [17]. The values of the Mo complexes are 3.98 (L = PBzImH) and 5.20 (PImH) in acetone/water (1:1 v/v). Compared with the molybdenum complexes, the ruthenium complexes described here have higher acid ionization constants pK_a, which indicate the stronger electron-donating ability of the $Ru(bpy)_2$ moiety than that of the $Mo(\eta\text{-}C_5H_5)_2$ moiety.

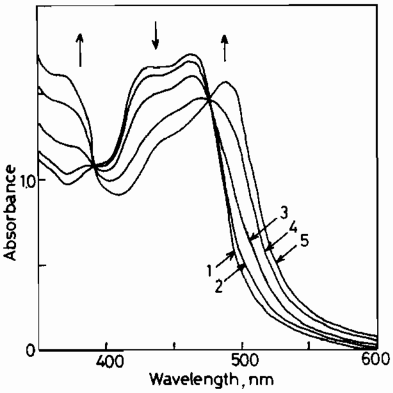

Fig. 1. Absorption spectra of $[Ru(bpy)_2(PImH)](ClO_4)_2$ (1.5×10^{-4} mol dm^{-3}) in 5% methanol/95% water solution at pH = 3.8(1), 6.3(2), 7.4(3), 8.4(4), and 10.8(5) at 25 °C.

Electrochemistry

The present Ru(II) complexes exhibit one oxidation and two reduction waves* in the cyclic voltammetry in acetonitrile, as listed in Table III. By comparing with the redox behaviour of $[Ru(bpy)_3]^{2+}$ and related complexes [18], the oxidation and the reductions are suggested to take place at the metal center and the bpy ligand π^* orbitals, respectively. The Ru(II) → Ru(III) oxidation potentials move cathodically in the order of OBzImH > $BiImH_2$ > $BiBzImH_2$ > PImH > PBzImH > bpy, which reflects the increasing donor property of the ligands. The two reduction waves at −1.5–−1.7 and −1.7–−2.0 V, both of which are reversible, are due to stepwise

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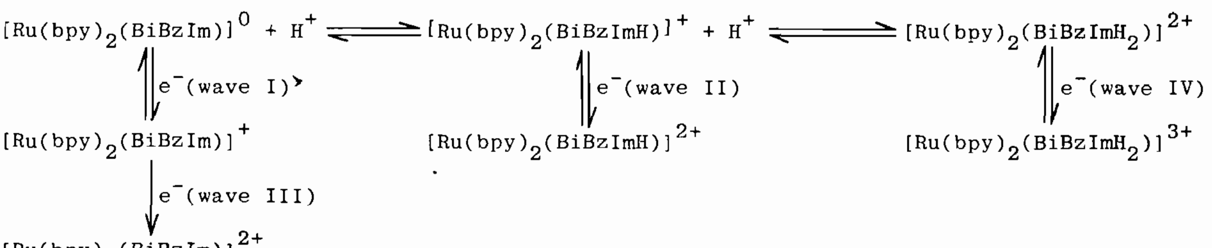
*In this series of ruthenium(II) complexes additional reduction waves were sometimes observed in the ranges of −0.7–−1.2 V *vs.* SCE, but these waves disappeared when cyclic voltammetric measurements were made in 'superdry' acetonitrile solutions suspending the neutral alumina. The trace water may induce the reduction processes in which the N–H bond probably participates. However, these reduction processes were not further pursued.



$$\begin{tikzcd}
{[Ru(bpy)_2(BiBzIm)]^0 + H^+} \arrow[d, leftrightarrows, "e^-(\text{wave I})"] & \rightleftharpoons & {[Ru(bpy)_2(BiBzImH)]^+ + H^+} \arrow[d, leftrightarrows, "e^-(\text{wave II})"] & \rightleftharpoons & {[Ru(bpy)_2(BiBzImH_2)]^{2+}} \arrow[d, leftrightarrows, "e^-(\text{wave IV})"] \\
{[Ru(bpy)_2(BiBzIm)]^+} \arrow[d, "e^-(\text{wave III})"] & & {[Ru(bpy)_2(BiBzImH)]^{2+}} & & {[Ru(bpy)_2(BiBzImH_2)]^{3+}} \\
{[Ru(bpy)_2(BiBzIm)]^{2+}} & & & &
\end{tikzcd}$$

Scheme 2.

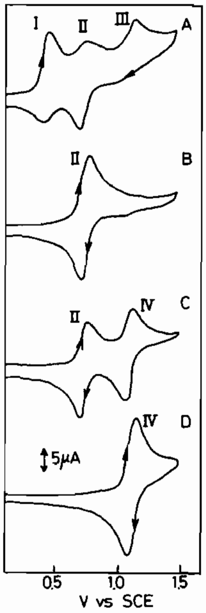


Fig. 2. Cyclic voltammograms of $[Ru(bpy)_2(BiBzIm)]^0$ (1.0×10^{-4} mol dm^{-3}) in acetonitrile containing 0.1 mol dm^{-3} TBAP as a supporting electrolyte and varying amounts of $HClO_4$: (A) 0, (B) 0.05, (C) 0.1, (D) 0.3 mmol dm^{-3}; scan rate of 100 mV/s.

TABLE IV. Cyclic Voltammetric Data for the Deprotonated $[Ru(bpy)_2L](ClO_4)_n$ Complexes.[a]

n	L	$E_{1/2}$[b], V *vs.* SCE	
		Oxidation	Reductions
1	PBzIm	+0.72(72)	−1.46(60), −1.70(63)
1	PImH	+0.76(irr)	−1.49(73), −1.73(56)
1	BiBzImH	+0.72(64)	−1.53(60), −1.86(80)
0	BiBzIm	+0.43(68)	−1.58(60), −1.87(60)
1	BiImH	+0.59(irr)	−1.64(67), −1.92(75)
0	BiIm	+0.20(irr)	−1.63(62), −1.92(68)
0	OBzIm	+0.09(60)	−1.63(60), −1.94(62)

[a]Measured in 0.1 mol dm^{-3} TBAP–acetonitrile by adding DBU. [b]$E_{1/2}$ values are the average of the anodic and cathodic peak potentials. The values in parentheses are the separation of anodic and cathodic peak potentials; irr = irreversible.

one-electron reductions at the bpy ligands. The cyclic voltammogram of deprotonated $[Ru(bpy)_2(PBzIm)]^+$ reveals one oxidation and two reduction waves. Compared with the potentials of the protonated $[Ru(bpy)_2(PBzImH)]^{2+}$, the oxidation potential is shifted by 0.46 V cathodically, while reduction potentials are unchanged. On the other hand, the deprotonated $[Ru(bpy)_2(BiBzIm)]$ in acetonitrile undergoes complicated oxidation steps (Fig. 2A). These oxidation waves were ascertained by the addition of aqueous $HClO_4$ to the solution of $[Ru(bpy)_2(BiBzIm)]$. The decrease of wave at +0.43 V (wave I) and +1.15 V (wave III, see Fig. 2A, B) and the increase of wave at +0.74 V (wave II, Fig. 2B) were observed initially. The further addition of $HClO_4$ results in appearance of a new wave IV and decrease of wave II (Fig. 2C). Finally only wave IV, which corresponds to the oxidation of protonated $[Ru(bpy)_2(BiBzImH_2)]^{2+}$, remained. This change of cyclic voltammograms can be interpreted by the stepwise protonation to the BiBzIm ligand coordinated to ruthenium, and electrode reactions for four waves I–IV can be assigned as in Scheme 2.

The cyclic voltammogram of $[Ru(bpy)_2(BiBzIm)]$ in acetonitrile (Fig. 2A) indicates the presence of a small amount of $[Ru(bpy)_2(BiBzImH)]^+$ in solution, which may be formed by the abstraction of a proton from trace amounts of water in acetonitrile. A similar protonation reaction has been reported for $[Ru(bpy)_2(pz)_2]$ (pz = pyrazolyl anion) [19].

When sodium methoxide or 1,8-diazabicyclo-[5,4,0]-7-undecene (DBU) was added in the solution of $[Ru(bpy)_2(PBzImH)]^{2+}$ or $[Ru(bpy)_2(BiBzImH_2)]^{2+}$, the cyclic voltammogram was identical with that of isolated deprotonated complex. Thus, the redox potentials for the other deprotonated complexes which have not been isolated were measured by the addition of DBU to the solution of complexes, which are compiled in Table IV. The deprotonation of the imidazole ligands results in the cathodic shifts

TABLE V. Excited State Properties of $[Ru(bpy)_2L](ClO_4)_2$.[a]

L	Solvent	Protonated λ_{max}, nm (lifetime, ns) room temperature	77 K	Deprotonated λ_{max}, nm room temperature	pK_a* (Calcd.)[b]
PBzImH	$MeOH-H_2O$[c]	630(262)		691	4.1
	EtOH–MeOH[d]	622(418)	600, 648(4240)		
PImH	$MeOH-H_2O$[c]	633(224)		690	5.2
	EtOH–MeOH[d]	625(160)	596, 647(4450)		
$BiBzImH_2$	$MeOH-H_2O$[e]	640(111)		705	2.6[f]
	EtOH–MeOH[d]	640(120)	616, 659(3000)		
$BiImH_2$	$MeOH-H_2O$[c]	656(92)		705	5.0[f]
	EtOH–MeOH[d]	651(150)	620, 663(3250)		
bpy[g]	H_2O	613, 627(600)			
	EtOH–MeOH		584, 628(5300)		

[a] The values obtained under the conditions of the emission titrations. [b] Calculated from the Forster cycles using the emission maxima and the value of pK_a. [c] In 5% methanol/95% water. [d] In ethanol–methanol (4:1 v/v). [e] In 50% methanol/50% water. [f] The pK_{a1}* value. [g] Ref. 23.

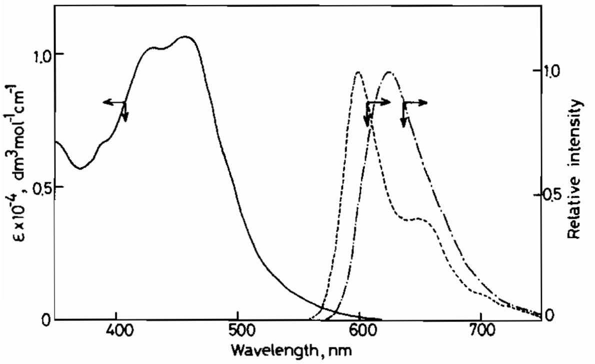


Fig. 3. Absorption spectrum of $[Ru(bpy)_2(PImH)](ClO_4)_2$ (———) in 5% methanol/95% water at room temperature and its emission spectra in ethanol-methanol (4:1 v/v) at room temperature (–·–·–) and 77 K (-----).

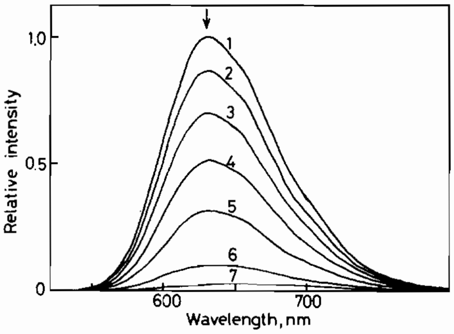


Fig. 4. Emission spectra of $[Ru(bpy)_2(PImH)](ClO_4)_2$ (6.8×10^{-5} mol dm^{-3}) exciting at 476 nm in 5% methanol/95% water solution at pH = 4.4(1), 7.5(2), 7.8(3), 8.30(4), 8.71(5), 9.12(6), and 10.4(7) at 25 °C.

of oxidation potential. This suggests that the electron density on the Ru ion increases as the result of a strong π-donor property of deprotonated ligands.

Emission Properties

The $[Ru(bpy)_2L]^{2+}$ complexes (L = PBzImH, PImH, $BiBzImH_2$, and $BiImH_2$) emit in solution at room temperature. When the temperature is lowered to 77 K the emission bands sharpen and exhibit vibrational structure (Fig. 3). However, $[Ru(bpy)_2(OBzImH)]^+$ does not emit both at room temperature and at 77 K. Emission spectral data for the complexes are given in Table V. The emission spectra of $[Ru(bpy)_2L]^{2+}$ complexes (L = PBzImH, PImH, $BiBzImH_2$, and $BiImH_2$) closely resemble that of $[Ru(bpy)_3]^{2+}$ [20], although the emission maxima are shifted to longer wavelengths. By analogy with the assignment for the luminescence of $[Ru(bpy)_3]^{2+}$ [20], the emissions in the 620–700 nm region are probably due to d–π* MLCT transition.

The emission lifetimes of $[Ru(bpy)_2L]^{2+}$ complexes are shorter than that of $[Ru(bpy)_3]^{2+}$ (Table V). The emission lifetimes decrease with increasing the number of imidazole or benzimidazole group in the ligand L. This decrease of lifetimes may be attributed to a rapid deactivation of the excited states, in which the excitation energy may be vibrationally dissipated to the solvent medium through the N–H bond of imidazole or benzimidazole ligand.

The emission spectra are strongly dependent on the pH values in solution. The emission intensities of the $[Ru(bpy)_2L]^{2+}$ complexes decrease and a slight red shift is observed with increasing the pH value; a representative emission spectral change is depicted in Fig. 4. The excited state acid ionization constants, pK_a^*, can be obtained by the following equation:

$$pK_a^* = pH_i + \log[\tau(\text{protonated})/\tau(\text{deprotonated})]$$

where the pH_i is the value of the pH at the inflection point in the emission titration curve and τ is the emission lifetime [21].

An attempt to measure the emission lifetime of the deprotonated complexes by the apparatus has unfortunately failed because the emission intensities of the deprotonated Ru complexes were too weak. Thus, the pK_a^* values are evaluated from the emission band maxima of protonated and deprotonaed forms in these complexes using Forster cycles [21], which are collected in Table V. It has been reported that the Forster cycle gives the precise pK_a^* values only in special cases, but it will at least indicate the direction of the pK_a-shift [21, 22]. The calculated pK_a^* values (Table V) qualitatively suggest that excited state species are stronger acids than the ground ones.

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