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Photoexcited States of Biruthenium(II) Compounds Bridged by 2,2'-Bis(2-pyridyl)bibenzimidazole or 1,2-Bis(2-(2-pyridyl)benzimidazolyl)ethane

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Charge-transfer (CT) excited states of $\text{RuL}_2(\text{L}'\text{-L}')^{2+}$ and $\text{RuL}_2(\text{L}'\text{-L}')^{4+}$ have been studied by means of emission and transient absorption (TA) spectroscopy at 77–300 K. The bridging ligand ($\text{L}'\text{-L}'$) is either 2,2'-bis(2-pyridyl)benzimidazole (bpbmH₂) or 1,2-bis(2-(2-pyridyl)benzimidazolyl)ethane (dpbime) and L is 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), or 1,10-phenanthroline (phen). Transient absorption (TA) spectra of the ruthenium(II) compounds subjected to laser excitation, whose molar extinction coefficients were determined, are deconvoluted to $\pi\text{-}\pi^*$ bands of L and $\text{L}'\text{-L}'$ coordinating to Ru(III), L (or $\text{L}'\text{-L}'$)-to-Ru(III) CT bands, and a $\pi\text{-}\pi^*$ band of $(\text{L}'\text{-L}')^{2+}$ (or L^{2+}) by comparison with the absorption spectra of the oxidized compounds ($\text{RuL}_2(\text{L}'\text{-L}')^{3+}$). The degree of electron population on the ligand decreases in the order $\text{bpbmH}_2 > \text{bpy} \sim \text{phen} > \text{dpbime} > \text{dmbpy}$ in the excited CT states, while there is no discernible difference in the reduction potential between bpbmH₂ (or dpbime) and bpy coordinating to Ru(II). The excitation efficiency of the metal sites in $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ is lower than 50% when the laser power was large enough to excite more than 80% of the mononuclear compounds. The low excitation efficiency of the former is ascribed to rapid intramolecular annihilation of the excited states.

Introduction

There has been considerable attention to the photochemical and photophysical properties of binuclear metal compounds bridged by ligands. Electronic interaction between the metal ions in the photoexcited (charge-transfer) states has been studied for biruthenium(II) diimine compounds having a symmetrical tetradentate bridge such as 2,3-bis(2-pyridyl)pyrazine (dpp),¹ 2,2'-bipyrimidine (bpym),² and 3,5-bis(pyridin-2-yl)-1,2,4-triazole (bpt).³ Coordination of the bridging ligands dpp and bpym to two ruthenium(II) ions resulted in a low-energy shift and shorter lifetime of metal-to-ligand charge-transfer (CT) luminescence. The lower energy shift of CT luminescence was attributed to the positive shift of the reduction potentials of dpp¹ and bpym² with coordination to the second Ru(II) ion. A splitting of the oxidation potentials of the equivalent ruthenium(II) ions suggested ruthenium–ruthenium superexchange interaction in the biruthenium(II) compound bridged by dpp, bpym, bpt, 2,2'-biimidazole,^{2b,4} or 2,2'-bibenzimidazole.⁵ The superexchange ruthenium–ruthenium interaction, which is expected for the metal-to-ligand CT excited state of the biruthenium(II) compounds, has not been clearly clarified.

Meanwhile, in the cases of binuclear compounds having 2,2'-bipyridines combined with a methylene chain⁶ or an amide chain⁷ as a bridging ligand, neither energy shift nor lifetime shortening of luminescence was observed in accordance with no shift of the redox potentials. Transfer processes of the excitation energy between the two metal sites, however, indicate the presence of weak electronic exchange interaction between Ru(II) ions in the excited and the ground states.⁸

Emission quenching of the metal chromophore in bichromophoric compounds via an electron-transfer mechanism has been studied,⁹ whose rates are strongly dependent on the strength of chromophore–chromophore interaction.¹⁰ Another factor determining the rate of the intramolecular processes was proposed to be the degree of population of the excited electron on the bridging ligand.¹¹ It was demonstrated that the electron population on the ligands in the CT excited state was highly dependent on the reduction potential of the bridging ligand relative to those of the other ligands.

Most recently, M.H. synthesized biruthenium(II) compounds bridged by a new type of tetradentate ligand, 2,2'-bis(2-pyridyl)bibenzimidazole (bpbmH₂),^{12a} in which 2-(2-pyridyl)benzimidazole (pbimH) moieties are combined by a phenyl–phenyl bond, as shown in Figure 1. The coordination of bpbmH₂ to Ru(II) ions was observed to give a very weak effect on the redox potential of $(\text{RuL}_2)_2(\text{bpbmH}_2)^{4+}$ compared with RuL_2 -

$(\text{bpbmH}_2)^{2+}$ (L = bpy for 2,2'-bipyridine). Coordination effect on the properties (energy and lifetime) of the CT excited state was examined over a wide temperature range (77–300 K). Though a preliminary study of transient absorption (TA) spectra of $\text{RuL}_2(\text{L}'\text{-L}')^{2+}$ and $(\text{RuL}_2)_2(\text{L}'\text{-L}')^{4+}$ (L: bpy, dmbpy for 4,4'-dimethyl-2,2'-bipyridine, phen for 1,10-phenanthroline) subjected

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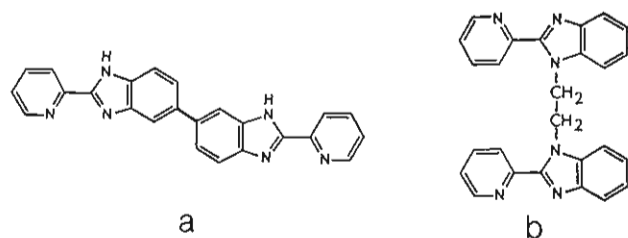


Figure 1. (a) 2,2'-bis(2-pyridyl)benzimidazole (bpbimH₂) and (b) 1,2-bis(2-(2-pyridyl)benzimidazolyl)ethane (dpbime).

to laser excitation has been done,^{12b} assignments of the TA bands are reinvestigated by comparing the absorption intensities of the TA with those of the Ru(III) compounds here. The π - π^* transition of bpbimH₂²⁻ is distinguished from both π - π^* of L coordinating to Ru(III) and L-to-Ru(III) CT, which were acquired by electrochemically oxidizing the Ru(II) compounds. The extent of electron population on bpbimH₂ in the CT excited state is estimated. Excited-state properties of another biruthenium(II) compound bridged by a ligand, 1,2-bis(2-(2-pyridyl)benzimidazolyl)ethane (dpbime),¹³ shown in Figure 1 is compared with those of (RuL₂)₂(bpbimH₂)⁴⁺. Occurrence of two dynamic processes, energy transfer and excited-state annihilation, between the ruthenium ions will be discussed.

Experimental Section

Materials. Phenothiazine supplied by Tokyo Kasei Co. was purified by vacuum sublimation. Acetonitrile was purified two times by distillation over P₂O₅. Tetra-*n*-butylammonium tetrafluoroborate ((TBA)-BF₄) and tetra-*n*-butylammonium perchlorate ((TBA)ClO₄) were recrystallized three times from ethyl acetate-pentane or ethanol-water mixtures and vacuum dried at 70 °C for 12 h. All other chemicals were of analytical grade and used as supplied.

Preparation. The compounds Ru(bpy)₂Cl₂·2H₂O, Ru(dmbpy)₂Cl₂·2H₂O, Ru(phen)₂Cl₂, [Ru(L)₂(bpbimH₂)](ClO₄)₂, and [Ru(L)₂](bpbimH₂)(ClO₄)₄ (L = bpy, phen, dmbpy) were prepared according to the literature.¹⁴ A bridging ligand, dpbime, was prepared and purified by following Lions and Martin.¹³

Preparation of Monomeric Complexes. [Ru(pbmH)]₃(ClO₄)₂. A suspension of RuCl₃·3H₂O (0.3 g, 1.3 mmol) in glycerol (20 cm³) was heated at 100 °C until the solution color became yellowish green (about 30 min-1 h). Solid pbmH (0.78 g, 4 mmol) was added to the resulting solution, and the mixture was heated for an additional 18 h. The reaction mixture was poured into an aqueous solution of NaClO₄ (1 g, 7.1 mmol), precipitating the red complex. The complex was purified by recrystallization from aqueous methanol. Yield: 0.66 g. Anal. Calcd for C₃₆H₂₇N₉RuCl₂O₈·2H₂O: C, 46.29; H, 3.43; N, 13.59. Found: C, 46.91; H, 3.39; N, 13.68.

[Ru(bpy)₂](dpbime)(ClO₄)₂. *cis*-Ru(bpy)₂Cl₂ (0.23 g, 0.47 mmol) in 1:1 ethanol-water (50 cm³) was heated for 30 min to give a red-violet solution. To the resulting solution was added solid dpbime (0.2 m, 0.48 mmol), and the mixture was refluxed for an additional 4 h, during which time the solution turned red-orange. The solution was concentrated to 10 cm³ and then filtered. Addition of a saturated aqueous NaClO₄ solution into the filtrate effected the precipitation of the complex. The product was purified by recrystallization from ethanol-water. Yield: 0.36 g (74%). Anal. Calcd for C₄₆H₃₆N₁₀RuCl₂O₈·H₂O: C, 52.78; H, 3.66; N, 13.38. Found: C, 52.78; H, 3.51; N, 13.36.

Preparation of Binuclear Complexes. [Ru(bpy)₂]₂(dpbime)(ClO₄)₄. Solid dpbime (0.15 g, 0.36 mmol) was added to a red-violet solution of Ru(bpy)₂Cl₂ (0.35 g, 0.72 mmol) in 1:1 ethanol-water (50 cm³), formed after heating for 30 min. The mixture was refluxed for 4 h, and the solution color changed from red-violet to red-orange. The solvent was evaporated to half-volume and then filtered. To the filtrate was added NaClO₄ (0.5 g, 4.1 mmol). The resulting orange precipitate was recrystallized from ethanol-water. For TA and the phosphorescence study, further purification was done by column chromatography on SP-Sephadex C-25 resin with 1:1 v/v acetonitrile-buffered water (pH 8.7) with addition of 5 mmol of NaClO₄. Yield: 0.4 g (68%). Anal. Calcd for C₆₆H₅₂N₁₄Ru₂Cl₂O₁₆·2H₂O: C, 46.27; H, 3.53; N, 11.45. Found: C, 45.64; H, 3.42; N, 11.22.

Preparation of Ru(III) Compounds. Ru(III) compounds were quantitatively prepared from the Ru(II) compounds by means of a flow-

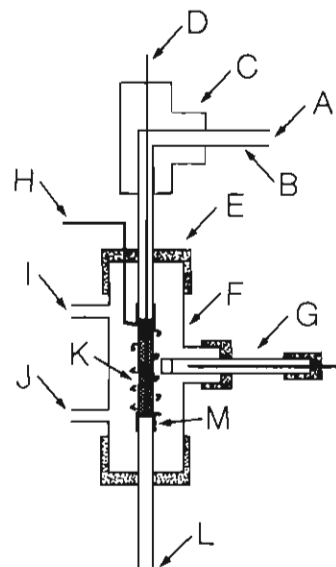


Figure 2. Scheme of a flow-through cell: (A) inlet of flowing solution; (B) Kel-F tube (2-mm o.d., 0.3-mm i.d.); (C) T-joint; (D) Pt lead wire (diameter 0.3 mm); (E) silicon rubber; (F) glass body; (G) reference electrode (I₃⁻/Pt); (H) Pt lead wire (diameter 0.2 mm); (I) inlet and (K) outlet of counter solution; (J) working electrode fabricated by packing carbon fibers tightly into a porous-glass diaphragm tube (1-mm i.d., 2-mm o.d., 30-mm length); (L) outlet of electrolyzed solution; (M) thermal shrinking tube.

electrolytic method.¹⁵ Figure 2 shows the construction of a flow-through cell used. An acetonitrile solution containing 0.1–0.5 mM Ru(II) compound and 0.1 M (TBA)ClO₄ was flowed into the cell at the flow rate of 0.4 mL/min. After being electrolyzed there, the sample solution was transferred to a quartz cell of 1- or 2-mm length. To minimize further chemical change of the Ru(III) compound, the spectra of Ru(III) compounds were observed within 10 min after oxidation. The working electrode potential higher than $E_{1/2}$ [Ru(III)/Ru(II)] by 0.3 V made 99.999% of the Ru(II) compound oxidized provided that electrochemical equilibrium in the flow-through cell was attained. Although the extent of oxidation was not evaluated for the Ru(II) compounds studied, 99% of Ru(phen)₃²⁺ was oxidized under the same conditions because the absorption at 460 nm due to the Ru(II) compound was diminished to 1% of the original. The flow rate of the solution was controlled by a computer-controlled dual pump (Tosoh, Tokyo, Japan). Controlled-potential electrolysis was carried out by using a DC pulse polarograph (HECS-312B, Huso, Kanagawa, Japan).

Apparatus. A Hitachi spectrofluorometer, Model MPF-2A, was used for phosphorescence spectra at 300 and 77 K. A Q-switched Nd³⁺-YAG laser (Quantel YG580) with the second harmonic light (532 nm) of 80 mJ was used for the excitation of Ru(II) compounds. A transmittance change acquisition system was described elsewhere.¹⁶ A xenon arc lamp (Hama Photonics, 150 W) was ca. 30 times intensified for 2 ms in order to improve the S/N ratio of photocurrent.

Measurements. The sample solutions of the ruthenium(II) compounds dissolved in acetonitrile or 1:4 methanol-ethanol were deaerated by bubbling with nitrogen more than 12 min. Either HClO₄ or CF₃COOH (1 mM) was added to suppress deprotonation of the imino groups of bpbimH₂, unless otherwise noted. TA spectra after exposure to the second harmonic pulse of the YAG laser were acquired by monitoring the absorbance change of the sample solution. A transient absorbance at 5–10-nm intervals of wavelength was obtained by averaging 3–8 measurements. Phosphorescence in the (12.8–17.5) × 10³ cm⁻¹ region was corrected for the transient absorption change. The energy of the 532-nm laser was attenuated by adding a solution filter consisting of chromium(III) alum. The temperature of the sample solutions in the 89–273 K region was controlled by using an Oxford DN1704 cryostat and an Oxford ITC4 controller.

The molar absorption coefficients of the excited ruthenium(II) compounds were evaluated by assuming 100% efficient energy transfer to anthracene.¹⁶ The formation of the triplet excited state of anthracene was determined by monitoring the triplet-triplet absorption at 421 nm

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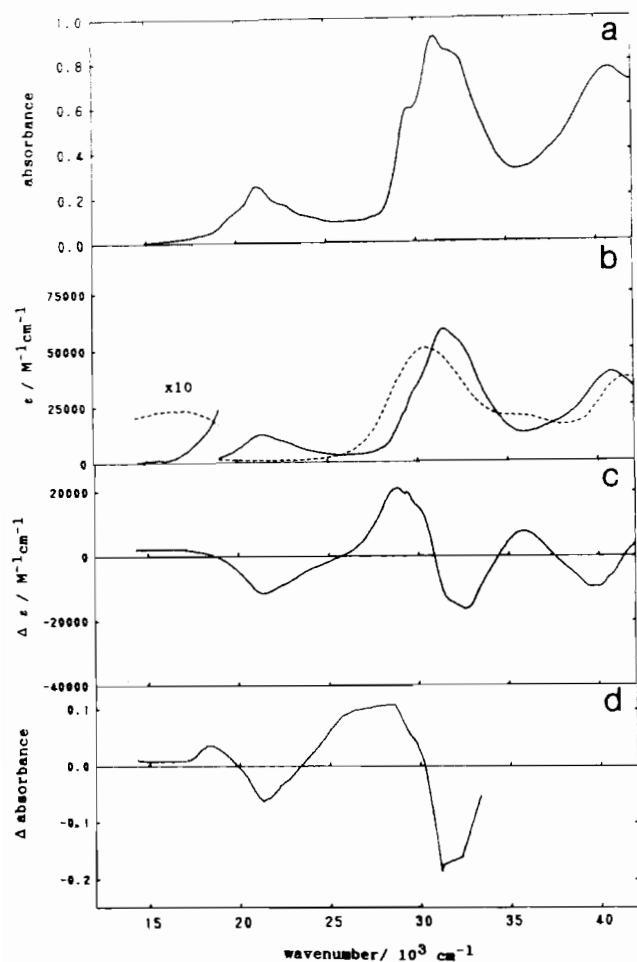


Figure 3. Absorption spectra of $\text{Ru}(\text{pbimH})_3^{2+}$: (a) $\text{Ru}(\text{pbimH})_3^{2+}$ ($5 \mu\text{M}$) in 1:4 methanol-ethanol at 90 K; (b) $\text{Ru}(\text{pbimH})_3^{2+}$ (solid line) and $\text{Ru}(\text{pbimH})_3^{3+}$ (broken line) in CH_3CN at ambient temperature; (c) difference (DA) spectrum with the oxidation of $\text{Ru}(\text{pbimH})_3^{2+}$; (d) TA spectrum of photoexcited $\text{Ru}(\text{pbimH})_3^{2+}$ ($5 \mu\text{M}$) in 1:4 methanol-ethanol at 120 K.

($\epsilon_{421} = 5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Rate constants of the energy-transfer processes were obtained by plotting the decay rate of CT emission against the concentration of anthracene added.

The DC pulse polarograph mentioned above was used for the measurements of redox potentials of Ru(II) compounds by means of differential-pulse voltammetry. All voltammograms were obtained at a platinum-disk electrode (diameter 0.5 mm) in CH_3CN containing 0.1 M (TBA)ClO₄. All potentials are referred to the formal potential of the ferrocenium (Fc^+)/ferrocene (Fc) system, which is +0.33 V vs SCE.

Results

1. Absorption Spectra of Ru(II) Compounds. Absorption spectra of $\text{Ru}(\text{pbimH})_3^{2+}$ and $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ at 90 K are shown in Figures 3a and 4a, respectively. Figure 5a also presents an absorption spectrum of $[\text{Ru}(\text{bpy})_2]_2(\text{bpbimH}_2)^{4+}$ at 90 K. Absorption spectra of the other compounds, including mononuclear compounds such as $\text{Ru}(\text{dmbpy})_2(\text{bpbimH}_2)^{2+}$ and $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$, at ambient temperature are shown in Figures 3b, 4b, 5b, 6a, and 7a. A $\pi-\pi^*$ band at $30 \times 10^3 \text{ cm}^{-1}$ of free bpbimH_2 is spread out $(27-32.2) \times 10^3 \text{ cm}^{-1}$ with small peaks at 27.5×10^3 and $30.5 \times 10^3 \text{ cm}^{-1}$ by forming the binuclear compounds. An unresolved charge-transfer (CT) band in the $(19-25) \times 10^3 \text{ cm}^{-1}$ region is seen for all mixed-ligand ruthenium(II) compounds studied here. The two kinds of CT bands, Ru(II)-to-bpy and Ru(II)-to- bpbimH_2 , are not distinguished even at 90 K.

2. Absorption Spectra of Ru(III) Compounds. A broad MLCT of the Ru(II) compound in the $(19-25) \times 10^3 \text{ cm}^{-1}$ region was

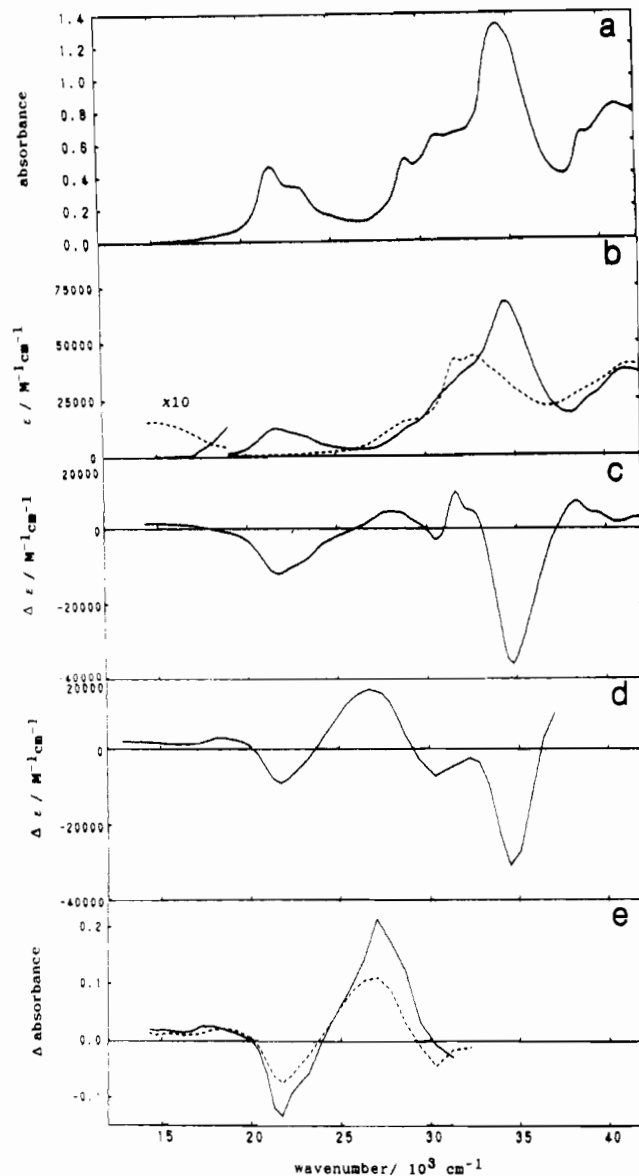


Figure 4. Absorption spectrum of $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$ and $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$: (a) $[\text{Ru}(\text{bpy})_2]_2(\text{bpbimH}_2)^{4+}$ ($12 \mu\text{M}$) in 1:4 methanol-ethanol at 90 K; (b) $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$ (solid line) and $\text{Ru}(\text{bpy})_2(\text{dpbime})^{3+}$ (broken line) in CH_3CN at ambient temperature; (c) DA with the oxidation of $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$; (d) TA of photoexcited $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ in CH_3CN at ambient temperature; (e) TA of photoexcited $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ ($20 \mu\text{M}$) in 1:4 methanol-ethanol at ambient temperature (broken line) and at 90 K (solid line).

completely bleached out with electrochemical oxidation of the compound, as shown in Figures 3-7. Broad bands of the compounds containing pbimH, dpbime, and bpbimH₂ in the red region are twice as intense ($\sim 2000 \text{ M}^{-1} \text{ cm}^{-1}$) as the L-to-Ru(III) CT bands of RuL_3^{3+} around $15 \times 10^3 \text{ cm}^{-1}$ ($400-1250 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁸ The strong $\pi-\pi^*$ bands of bpy, dmbpy, and phen are shifted to $32 \times 10^3 \text{ cm}^{-1}$ with the oxidation of the Ru(II) compounds. The strong $\pi-\pi^*$ bands of pbimH ($31.3 \times 10^3 \text{ cm}^{-1}$), dpbime ($31.3 \times 10^3 \text{ cm}^{-1}$), and bpbimH₂ ($27.8 \times 10^3 \text{ cm}^{-1}$) are not much affected by the oxidation of the Ru(II) ion.

3. Emissions of Ru(II) Compounds. Each of the ruthenium(II) compounds exhibited a long-life emission in the red ($12.8-16.8$)

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(18) The molar absorption coefficients of the broad bands in the red region were determined to be $400 \text{ M}^{-1} \text{ cm}^{-1}$ for L = bpy, $450 \text{ M}^{-1} \text{ cm}^{-1}$ for L = dmbpy, and $1250 \text{ M}^{-1} \text{ cm}^{-1}$ for L = phen. Though these are in agreement with the previously reported values (McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428-41), the whole absorption spectra of RuL_3^{3+} are substantially different. The details of the spectra will be reported elsewhere.

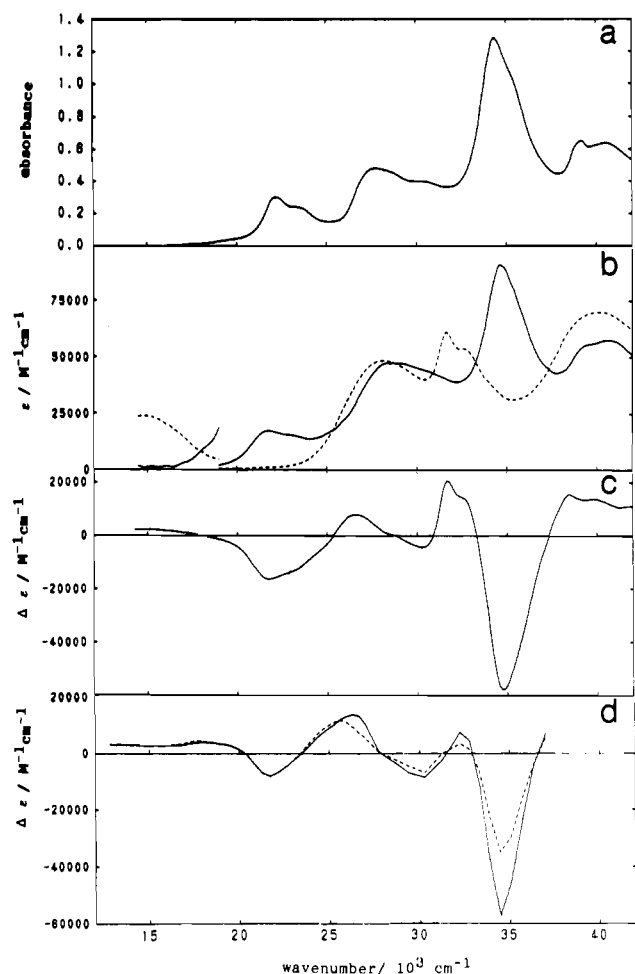


Figure 5. Absorption spectra of $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$ and $[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{4+}$: (a) $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$ (8.8 μM) in 1:4 methanol-ethanol at 90 K; (b) $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$ (solid line) and $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{3+}$ (broken line) in CH_3CN at ambient temperature; (c) DA with the oxidation of $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$; (d) TA of photoexcited $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$ (solid line) and $[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{4+}$ (broken line) in CH_3CN at ambient temperature.

Table I. Highest Energy Bands of Emissions at 77 K and Lifetimes of Emissions at 90 K and at Ambient Temperature

	ν/cm^{-1} ^a	$\tau/\mu\text{s}$ ^b	$\tau/\mu\text{s}$ ^c
$\text{Ru}(\text{pbimH})_3^{2+}$	15 500 (1.921)	0.087	0.47 ^d
$\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$	16 530 (2.049)	0.42	
$\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$	16 500 (2.045)	0.48	
$\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)^{2+}$	16 290 (2.019)	0.45	
$\text{Ru}(\text{phen})_2(\text{bpimH}_2)^{2+}$	16 700 (2.070)	0.54	4.94
$[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$	16 440 (2.041)	0.99	3.03
$[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{4+}$	16 370 (2.029)	0.56	2.77
$[\text{Ru}(\text{dmbpy})_2]_2(\text{bpimH}_2)^{4+}$	16 070 (1.992)	0.48	2.22
$\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)\text{Ru}(\text{phen})_2^{4+}$	15 950 (1.977)	0.48	

^a Numbers in parentheses denote emission energy in eV. ^b In CH_3CN at ambient temperature. ^c In 1:4 methanol-ethanol at 90 K. ^d In 1:4 methanol-ethanol at 123 K.

$\times 10^3 \text{ cm}^{-1}$) region at 77 K. Raising the temperature shifted the band peaks to longer wavelength and shortened the lifetimes. The highest energy peaks of the emissions at 77 K are listed together with the lifetimes at ambient temperature and 90 K in Table I.

4. Transient Absorption (TA) Spectra. A transient difference absorption (TA) spectrum at 120 K was obtained 100 ns after 532-nm laser excitation of $\text{Ru}(\text{pbimH})_3^{2+}$, as is shown in Figure 3d. The TA decayed with the same rate as the phosphorescence monitored at $15 \times 10^3 \text{ cm}^{-1}$. Therefore, the TA is ascribed to the formation of an excited MLCT state emitting phosphorescence.

Figure 4 shows TA spectra of $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ in CH_3CN at ambient temperature and in 4:1 ethanol-methanol at

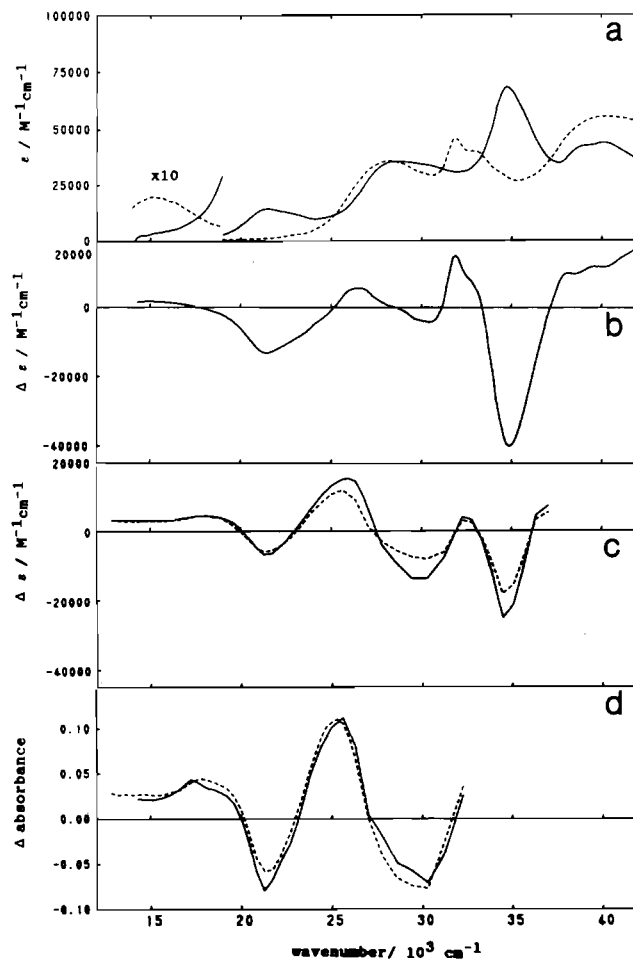


Figure 6. Absorption spectra of $\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)^{2+}$ and $[\text{Ru}(\text{dmbpy})_2]_2(\text{bpimH}_2)^{4+}$: (a) $\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)^{2+}$ (solid line) and $\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)^{3+}$ (broken line) in CH_3CN at ambient temperature; (b) DA with the oxidation of $\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)^{2+}$; (c) TA of photoexcited $\text{Ru}(\text{dmbpy})_2(\text{bpimH}_2)^{2+}$ (broken line) and $[\text{Ru}(\text{dmbpy})_2]_2(\text{bpimH}_2)^{4+}$ (solid line) in CH_3CN at ambient temperature; (d) TA spectra of $[\text{Ru}(\text{dmbpy})_2]_2(\text{bpimH}_2)^{4+}$ (20 μM) in 1:4 methanol-ethanol at ambient temperature (broken line) and at 90 K (solid line).

90 K. The difference in molar absorption coefficient between the ground state and the excited state, $\Delta\epsilon$, was determined by utilizing a bimolecular energy-transfer process. The rate constants of Ru(II)-to-anthracene energy transfer are listed together with $\Delta\epsilon$ at the absorption peaks in Table II. TA spectra of $\text{RuL}_2(\text{bpimH}_2)^{2+}$ and $[\text{RuL}_2]_2(\text{bpimH}_2)^{4+}$ ($\text{L} = \text{bpy}, \text{dmbpy}$) were similarly obtained (Figures 5d and 6c) in the presence of HClO_4 (1 mM), which suppressed deprotonation from the NH groups of bpimH_2 . The TA of $[\text{Ru}(\text{dmbpy})_2]_2(\text{bpimH}_2)^{4+}$ decayed in biphasic; the slow decay component exhibited the same lifetime as phosphorescence. A TA spectrum of $\text{Ru}(\text{phen})_2(\text{bpimH}_2)^{2+}$ in CH_3CN at ambient temperature is given in Figure 7.

The addition of an electron donor, phenothiazine (0.8 mM), quenched the TA of $\text{Ru}(\text{phen})_2(\text{dpbime})^{2+}$ to produce another transient absorption spectrum in 6 μs (Figure 7d).

5. Electrochemistry. Redox potentials of the ruthenium(II) compounds were obtained as shown in Table III. Redox potentials were measured as $E_{1/2}$ values by means of differential-pulse voltammetry. Reduction potentials of $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$, $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$, $[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{4+}$, and $[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{2+}$ were measured as $E_{1/2}$ values by cyclic voltammetry. The first reduction process of the bpimH_2 coordinating compounds along with other binuclear compounds is irreversible, as shown in Figure 8.

6. Laser-Power Dependence of Excited-State Formation. Production of the excited state of $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ (15 μM) was measured with attenuation of the laser power (Figure 9). The

Table II. Difference Molar Absorption Coefficients of Transient Absorption (TA) Bands of Ruthenium(II) Compounds and Rate Constants ($k/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$) of Energy-Transfer Processes to Anthracene in CH_3CN

	$\Delta\epsilon/\text{M}^{-1} \text{cm}^{-1}$ at wavenumber/ 10^3cm^{-1}					$k/10^9$
	34.8	30.0	24.6	22.0	14.3	
$\text{Ru}(\text{bpy})_3^{2+ a}$	-70 000	13800 ^b	17 500 ^c	-9800	1500	4.7
$\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$	-39 400		14 600 ^c	-9240	1650	2.56
$[\text{Ru}(\text{bpy})_2]_2(\text{bpbime})^{4+}$	-34 700		16 300 ^c	-9100	1900	1.46
$\text{Ru}(\text{bpy})_2(\text{bpbimH}_2)^{2+}$	-37 000	-7300	12 300	-6730	3000	4.0
$[\text{Ru}(\text{bpy})_2]_2(\text{bpbimH}_2)^{4+}$		-5300	12 000	-6780	2900	1.85
$\text{Ru}(\text{dmbpy})_3^{2+ a}$		11200	14 800	-9300	1570	9.0
$\text{Ru}(\text{dmbpy})_2(\text{bpbimH}_2)^{2+}$	-35 400	-9900	15 100	-6750	3500	3.14
$[\text{Ru}(\text{dmbpy})_2]_2(\text{bpbimH}_2)^{4+}$						2.24
$\text{Ru}(\text{phen})_3^{2+ a}$		9500		-14400	1650	7.4
$\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$		-4500	8 050	-7500	2900	4.88

^a Reference 24. ^b At $32.2 \times 10^3 \text{cm}^{-1}$. ^c At $27 \times 10^3 \text{cm}^{-1}$.

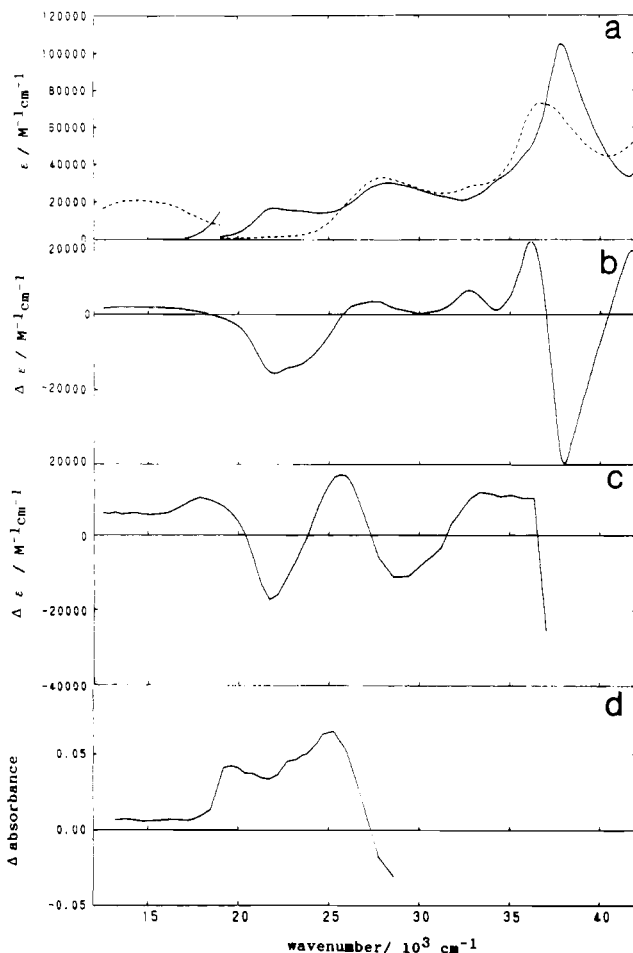


Figure 7. Absorption spectra of $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$: (a) $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$ (solid line) and $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{3+}$ (broken line) in CH_3CN at ambient temperature; (b) DA with the oxidation of $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$; (c) TA of photoexcited $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$ in CH_3CN at ambient temperature; (d) TA of photoexcited $\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$ (20 μM) in the presence of phenothiazine (0.8 mM) in CH_3CN at ambient temperature 6 μs after the laser excitation.

fraction of the Ru(II) site excited was below 50% for excitation with a laser power of 80 mJ. In the case of the monoruthenium compound (30 μM) with the same absorbance at 532 nm as that of the biruthenium compound, 80% of Ru(II) was excited for excitation with the same laser power.

Discussion

1. Reduction Potentials. Mononuclear $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$ shows one reversible oxidation wave and four reversible reduction waves in CH_3CN , each of which is a one-electron process. Binuclear $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ exhibits one reversible oxidation wave and three closely located reversible reduction waves, each of which is associated with a one-electron process. The oxidation

Table III. Redox Potentials of Ruthenium(II) Compounds vs Fc^+/Fc in CH_3CN Containing 0.1 M Tetraethylammonium Perchlorate

	$E_{1/2}(\text{Ru(II)}/\text{Ru(III)})/\text{mV}$	$E_{1/2}(\text{L}/\text{L}^-)/\text{mV}$		
$\text{Ru}(\text{bpy})_3^{2+}$	875	-1724	-1913	-2167
$\text{Ru}(\text{pbimH}_2)^{2+}$	550			
$\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$	780 (776) ^a	-1732	-1921	-2169
$[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$	830 (793) ^a	-1714	-1918	-2180
$\text{Ru}(\text{bpy})_2(\text{bpbimH}_2)^{2+}$	777			
$[\text{Ru}(\text{bpy})_2]_2(\text{bpbimH}_2)^{4+}$	777	-1780 ^b	-1875 ^c	-2145 ^c
$[\text{Ru}(\text{bpy})_2]_2(\text{bpbim})^{2+}$	347		-1846	-2100
$\text{Ru}(\text{dmbpy})_3^{2+}$	714	-1829	-2013	-2246
$\text{Ru}(\text{dmbpy})_2(\text{bpbimH}_2)^{2+}$	680			
$[\text{Ru}(\text{dmbpy})_2]_2(\text{bpbimH}_2)^{4+}$	680			
$\text{Ru}(\text{phen})_3^{2+}$	900	-1758	-1960	-2210
$\text{Ru}(\text{phen})_2(\text{bpbimH}_2)^{2+}$	775			

^a Numbers in parentheses give $E_{1/2}$ values in butyronitrile. ^b Irreversible wave. ^c With an error of 30 mV.

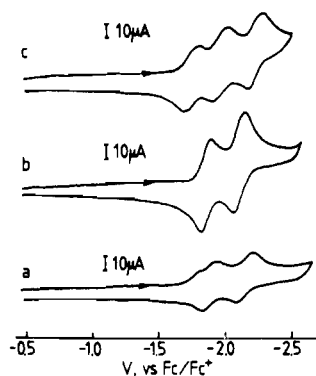


Figure 8. Reductive cyclic voltammograms of binuclear Ru(II) compounds in CH_3CN containing 0.1 M of $(\text{TBA})\text{BF}_4$ at a glassy-carbon electrode (scan rate = 100 mV s^{-1}): (a) $[\text{Ru}(\text{bpy})_2]_2(\text{bpbimH}_2)^{4+}$ (0.3 mM); (b) $[\text{Ru}(\text{bpy})_2]_2(\text{bpbim})^{2+}$ (0.5 mM); (c) $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ (0.5 mM).

process is Ru(II)/Ru(III) metal-based, while the reduction processes are associated with the ligand π^* LUMO energies. In the present system, the potential values and pattern of the reduction are quite close to those of $\text{Ru}(\text{bpy})_3^{2+}$. Thus, it is difficult to assign the reduction sites only by using electrochemical methods. The potential difference between the binuclear and mononuclear dpbime compounds is quite small. This result indicates that the metal-metal interaction might be very small.

For the bpbimH₂ compound, the oxidation potential for binuclear compounds is identical to that of the mononuclear compound (Table III). In the reduction processes for binuclear bpbimH₂ compound, two main waves at -1.87 and -2.14 V vs Fc^+/Fc in addition to an irreversible wave at -1.78 V (scan rate = 100 mV s^{-1}) were observed (see Figure 8); however, the absorption on the electrode complicates the assignment of these reduction processes. When the bpbimH₂ bridging moiety is dideprotonated, two

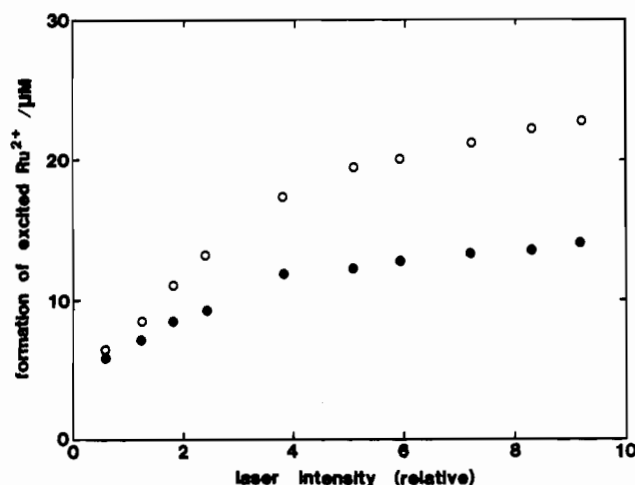


Figure 9. Dependence of the production of the excited state on the laser intensity in CH_3CN : (O) $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$ ($30 \mu\text{M}$) and (●) $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ ($15 \mu\text{M}$) at ambient temperature.

well-defined reduction waves at -1.85 and -2.10 V vs Fc^+/Fc are observed. Since the deprotonation of bpbimH_2 destabilizes the π^* orbital energies of bpbimH_2 , these two reduction processes can be assigned as bpy ligand-centered. Thus, the irreversible wave observed for the protonated bpbimH_2 compound is bpbimH_2 ligand-based, and π^* orbital energies of bpbimH_2 may be located near that of bpy .

Characteristic of the bpbimH_2 binuclear compound is a small potential shift on changing from the mononuclear to the binuclear compound, compared to a large potential shift observed for the dpp - and bpym -bridging compounds and their analogues.^{1,2}

2. Assignments of Absorption and Emission Bands. $\text{Ru}(\text{pbimH})_3^{2+}$ exhibits a poorly resolved absorption spectrum at 90 K (Figure 3a). The $\text{Ru}(\text{II})$ -to- pbimH CT transition at $19.7 \times 10^3 \text{ cm}^{-1}$ is of low energy compared with that for $\text{Ru}(\text{bpy})_3^{2+}$ ($22.1 \times 10^3 \text{ cm}^{-1}$)¹⁹ or $\text{Ru}(2-(2'-\text{pyridyl})\text{imidazole})_3^{2+}$ ($22.8 \times 10^3 \text{ cm}^{-1}$),²⁰ and the other bands at 30.0×10^3 , 31.0×10^3 , 32.2×10^3 , and $40.8 \times 10^3 \text{ cm}^{-1}$ are assigned to $\pi-\pi^*$ transitions of pbimH . The emission peak at $15.5 \times 10^3 \text{ cm}^{-1}$ is of low energy compared with the CT phosphorescence of $\text{Ru}(\text{bpy})_3^{2+}$ ($17.1 \times 10^3 \text{ cm}^{-1}$)¹⁹ and $\text{Ru}(2-(2'-\text{pyridyl})\text{imidazole})_3^{2+}$ ($17.0 \times 10^3 \text{ cm}^{-1}$).²⁰ The lower energy emission compared to that of $\text{Ru}(\text{bpy})_3^{2+}$ by 300 meV can be accounted for by the difference (300 mV) in the oxidation potential between $\text{Ru}(\text{pbimH})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$.

As for $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ (Figure 4a), a transition of Ru -to- dpbime CT seems to be hidden by a series of bands characteristic of Ru -to- bpy CT (21.8×10^3 , 23.5×10^3 , and $\sim 25 \times 10^3 \text{ cm}^{-1}$). The bands in a UV region are ascribed to dpbime (29.3×10^3 , 31.1×10^3 , 32.2×10^3 , and $40.8 \times 10^3 \text{ cm}^{-1}$) and to bpy (34.5×10^3 and $39 \times 10^3 \text{ cm}^{-1}$). The broad CT band of $[\text{Ru}(\text{bpy})_2]_2(\text{bpbimH}_2)^{4+}$ in the $(20-25) \times 10^3 \text{ cm}^{-1}$ region of Figures 5a, whose peak was slightly shifted to lower energy ($(21.7-21.5) \times 10^3 \text{ cm}^{-1}$) on lowering the temperature, suggests superposition of Ru -to- bpy CT and Ru -to- bpbimH_2 CT. The broader bands at $\sim 27.5 \times 10^3$ and $\sim 30.6 \times 10^3 \text{ cm}^{-1}$ can be referred to as $\pi-\pi^*$ transitions of bpbimH_2 .

The lower energy phosphorescences of both $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$ and $\text{Ru}(\text{bpy})_2(\text{bpbimH}_2)^{2+}$ compared to that of $\text{Ru}(\text{bpy})_3^{2+}$ do not imply the emission originates from Ru -to- dpbime or Ru -to- bpbimH_2 CT. The less positive oxidation potentials reduce both the energies of the CT states. Assignments of the reduced ligand in the excited CT states will be made by the aid of a TA spectrum.

3. Identification of a Reduced Ligand in the $\text{Ru}(\text{II})$ -to-Ligand CT Excited State. The $\text{Ru}(\text{II})$ -to-L CT excited state has been

regarded as an anion radical of a ligand coordinating to $\text{Ru}(\text{II})$.²¹⁻²⁴ The electronic absorption spectra of excited CT states of $\text{RuL}'_2\text{L}^{2+}$ consist of (1) $\pi-\pi^*$ transitions of the reduced ligand (L'^-), (2) $\pi-\pi^*$ transitions of L' coordinating to $\text{Ru}(\text{III})$, and (3) LMCT transitions of L' -to- $\text{Ru}(\text{III})$ and L'^- -to- $\text{Ru}(\text{III})$.^{23d,f} Therefore, TA spectra, as well as the transient Raman spectra,^{21,22} have been utilized for identification of the reduced ligand in the excited CT state.^{23,24}

$\text{Ru}(\text{pbimH})_3^{2+}$, $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$, and $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$. The TA spectrum of $\text{Ru}(\text{pbimH})_3^{2+}$ subjected to laser excitation (Figure 3d) exhibits two bleached bands at 21.7×10^3 and $31.2 \times 10^3 \text{ cm}^{-1}$ and two enhanced ones in the violet and a red regions, respectively. By comparison with a difference absorption (DA) band in the $(25.6-30) \times 10^3 \text{ cm}^{-1}$ region obtained by the oxidation of $\text{Ru}(\text{pbimH})_3^{2+}$ (Figure 3c), the wide TA band in the $(24-30) \times 10^3 \text{ cm}^{-1}$ region is deconvoluted to the shifted $\pi-\pi^*$ band of pbimH coordinating to $\text{Ru}(\text{III})$ at $28.6 \times 10^3 \text{ cm}^{-1}$ and a new band centered at $\sim 26 \times 10^3 \text{ cm}^{-1}$, the latter of which can be assigned to a $\pi-\pi^*$ transition of pbimH^- . A much wider TA band in the red region can be ascribed to LMCT because of the similarly broad band of $\text{Ru}(\text{pbimH})_3^{3+}$. A small peak at $18.5 \times 10^3 \text{ cm}^{-1}$ is assigned to a $\pi-\pi^*$ band of pbimH^- .

A mixed-ligand complex $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ (Figure 4d,e) exhibits a hybrid of the TA spectra of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{pbimH})_3^{2+}$ (Figure 3d). Formation of bpy^- is evident because of the high TA band at $27 \times 10^3 \text{ cm}^{-1}$ (see Table II), while the similarly strong band of excited $\text{Ru}(\text{bpy})_3^{2+}$ at $32.2 \times 10^3 \text{ cm}^{-1}$ ^{23d,23f,24} is indistinct. Formation of dpbime^- is also led by appearance of the band at $18.5 \times 10^3 \text{ cm}^{-1}$ and by loss of the $\pi-\pi^*$ band of dpbime around $30 \times 10^3 \text{ cm}^{-1}$, the latter of which was much more than the absorbance loss at $30 \times 10^3 \text{ cm}^{-1}$ in the DA spectrum obtained by the oxidation of $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ (Figure 4c). Coexistence of bpy^- and dpbime^- in the CT excited state is consistent with the three closely located one-electron electrochemical processes. Lowering the temperature of $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ in 1:4 methanol-ethanol enhanced the peak absorbance at $27 \times 10^3 \text{ cm}^{-1}$ substantially. Meanwhile, the absorbances at $18.5 \times 10^3 \text{ cm}^{-1}$ and around $25 \times 10^3 \text{ cm}^{-1}$ (Figure 4e), which can be ascribed not to bpy^- but to dpbime^- , did not change their intensities. These temperature dependences of the band intensities can be accounted for by increased population of the transferred electron on bpy at the lower temperatures. The energy difference between bpy^- and dpbime^- is estimated to be as big as kT (24 meV). The TA spectrum of $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ is almost identical to that of the mononuclear counterparts.

$\text{RuL}_2(\text{bpbimH}_2)^{2+}$ and $[\text{RuL}_2]_2(\text{bpbimH}_2)^{4+}$ ($\text{L} = \text{bpy}, \text{dmbpy}, \text{phen}$). The bridging bpbimH_2 is expected to be a somewhat better electron acceptor than pbimH and dpbime , because an energy shift of the $\pi-\pi^*$ transition from $30.0 \times 10^3 \text{ cm}^{-1}$ to $27.5 \times 10^3 \text{ cm}^{-1}$ suggests a pbimH - bpbimH interaction lowering the π^* level of bpbimH_2 . TA spectra of $\text{RuL}_2(\text{bpbimH}_2)^{2+}$ and $[\text{RuL}_2]_2(\text{bpbimH}_2)^{4+}$ ($\text{L} = \text{bpy}, \text{dmbpy}$) in CH_3CN (Figures 5d and 6c) exhibit bleached bands at 34.8×10^3 , $\sim 30.5 \times 10^3$, and $21.7 \times 10^3 \text{ cm}^{-1}$ and enhanced bands at 25.6×10^3 , 32.2×10^3 , and <20

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$\times 10^3 \text{ cm}^{-1}$. Appearance of either $\text{bpy}^{\cdot-}$ or $\text{bpbimH}_2^{\cdot-}$ is responsible for the diminished bleaching of TA at 21.7×10^3 and $34.8 \times 10^3 \text{ cm}^{-1}$ compared to the DA spectra (Figures 5c and 6b) obtained by the oxidation of the Ru(II) compound. The increased bleaching at $30.5 \times 10^3 \text{ cm}^{-1}$ compared with that for the oxidation implies that the greater bleaching of the $\text{bpbimH}_2 \pi-\pi^*$ band is caused by the conversion of bpbimH_2 to $\text{bpbimH}_2^{\cdot-}$. The weakly positive band at $32.2 \times 10^3 \text{ cm}^{-1}$ ($\Delta\epsilon \sim 3500 \text{ M}^{-1} \text{ cm}^{-1}$), which arises from the shifted $\pi-\pi^*$ band of bpy coordinating to Ru(III), indicates the conversion of bpbimH_2 to $\text{bpbimH}_2^{\cdot-}$. The absorbance change at $25.6 \times 10^3 \text{ cm}^{-1}$ ($12\,000\text{--}15\,000 \text{ M}^{-1} \text{ cm}^{-1}$) on CT excitation can be taken as evidence for the formation of $\text{bpbimH}_2^{\cdot-}$, while the oxidation of the compound shifted the $\pi-\pi^*$ band of bpbimH_2 resulting in the enhanced absorbance of $1300\text{--}3000 \text{ M}^{-1} \text{ cm}^{-1}$ at $25.6 \times 10^3 \text{ cm}^{-1}$ (see Figure 6b). The TA band of $\text{bpy}^{\cdot-}$ or $\text{dmbpy}^{\cdot-}$ at $27 \times 10^3 \text{ cm}^{-1}$,^{23,24} whose peak is not obvious in Figures 5d and 6c, might enhance the absorbance at $25.6 \times 10^3 \text{ cm}^{-1}$ too.

The band at $25.6 \times 10^3 \text{ cm}^{-1}$ was also found for excited Ru(phen)₂(bpbimH_2)²⁺ in CH_3CN (Figure 7c). The band at $25.6 \times 10^3 \text{ cm}^{-1}$ originates neither from the shifted $\pi-\pi^*$ band of phen coordinating to Ru(III) nor the $\pi-\pi^*$ band of phen^{•-}. DA bands obtained by the oxidation of Ru(phen)₂(bpbimH_2)²⁺ in the ultraviolet region do not appear at $25.6 \times 10^3 \text{ cm}^{-1}$ but at $\sim 28 \times 10^3$ and $33 \times 10^3 \text{ cm}^{-1}$. Therefore, it is concluded that the band of excited Ru(phen)₂(bpbimH_2)²⁺ at $25.6 \times 10^3 \text{ cm}^{-1}$ ($\Delta\epsilon = 8050 \text{ M}^{-1} \text{ cm}^{-1}$) fully comes from the anion radical of bpbimH_2 . A TA band at $33 \times 10^3 \text{ cm}^{-1}$ observed for Ru(phen)₂(bpbimH_2)²⁺ ($\Delta\epsilon = 5900 \text{ M}^{-1} \text{ cm}^{-1}$) could originate from both the $\pi-\pi^*$ transition of phen coordinating to Ru(III) ($\Delta\epsilon = 6500 \text{ M}^{-1} \text{ cm}^{-1}$ in Figure 7b) and that of phen^{•-} ($\Delta\epsilon = 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$).²⁵ If the excited electron resides on phen, $\Delta\epsilon$ of TA at $33 \times 10^3 \text{ cm}^{-1}$ should be the sum of the two values, $17\,000 \text{ M}^{-1} \text{ cm}^{-1}$. The smaller value of $\Delta\epsilon$ observed demonstrates preferential population of the electron on bpbimH_2 in the CT state.

The absorption band of the CT excited state at $25.6 \times 10^3 \text{ cm}^{-1}$ was compared with the TA band of the chemically reduced form of Ru(phen)₂(bpbimH_2)²⁺ (Figure 7d). Electron-transfer quenching of ³Ru(phen)₂(bpbimH_2)²⁺ by phenothiazine (0.8 mM) produces three absorption peaks at 19.2×10^3 , 22.7×10^3 , and $25.6 \times 10^3 \text{ cm}^{-1}$, of which the first two bands and the last one are assigned to the cation radicals of phenothiazine²⁶ and Ru(phen)₂($\text{bpbimH}_2^{\cdot+}$), respectively.

The broad bands of the excited RuL₂(bpbimH_2)²⁺ in the red region are more intense ($\epsilon = 2900\text{--}3500 \text{ M}^{-1} \text{ cm}^{-1}$) than those of RuL₃³⁺ (L = bpy, dmbpy, phen), which are mostly explained both by the $\pi-\pi^*$ band of $\text{bpbimH}_2^{\cdot-}$ and by $\text{bpbimH}_2^{\cdot-}$ -to-Ru(III) CT. The same TA of [Ru(dmbpy)₂]₂(bpbimH_2)⁴⁺ in the alcoholic solvent at 90 K as in CH_3CN at ambient temperature demonstrates that the excited electron exclusively resides on bpbimH_2 .

The energy of the Ru(II)-to-L CT phosphorescent state of the monoruthenium compound can be expressed by the following equation:

$$h\nu = E^\circ(\text{Ru(III)}/\text{Ru(II)}) - E^\circ(\text{L}/\text{L}^{\cdot-}) - \text{EE} \quad (1)$$

Here EE is the sum of the electrostatic energy and electronic exchange energy between Ru(III) and a reduced ligand. In the mixed-ligand complex of RuL₂L²⁺, the excited electron resides on L of which $E^\circ(\text{L}/\text{L}^{\cdot-})$ is less negative, provided that the EE values are nearly constant irrespective of the ligands. The preferential population of an electron on bpbimH_2 in the CT excited state of RuL₂(bpbimH_2)²⁺ indicates the less negative potential of bpbimH_2 compared to that of bpy, while the presence of a nonreversible redox process enable us to unambiguously determine $E^\circ(\text{L}/\text{L}^{\cdot-})$ for bpbimH_2 . The more negative reduction potential of Ru(dmbpy)₃²⁺ compared with those of Ru(bpy)₃²⁺ and Ru(phen)₃²⁺ by more than 100 mV is consistent with the order in the degree of the electron occupation on the ligands in the CT

excited state, $\text{bpbimH}_2 > \text{bpy} \sim \text{phen} > \text{dmbpy}$.

4. Interaction between Ruthenium(II) Sites of Excited Binuclear Compounds. Three kinds of chromophore-chromophore interactions are possible in the excited Ru-to-L CT of [RuL₂]₂(L^{•-})⁴⁺, superexchange interactions between Ru(II) in the ground state and Ru(III) ions in the excited state and between Ru(III) ions in the excited state. The third interaction between a ligand and a reduced ligand is not very weak but sufficient to transfer the excited electron between ligands within several pico seconds.^{11,21,22,27}

The phosphorescence of the biruthenium compounds at 77 K were observed to decrease by 16 and 27 meV for [RuL₂]₂(bpbimH_2)⁴⁺ (L = bpy, dmbpy), respectively, compared to the monoruthenium counterparts. The small energy shifts of the phosphorescences exceeding experimental error are not accounted for by the shift of redox potentials of [RuL₂]₂(bpbimH_2)⁴⁺ (L = bpy, dmbpy) available. The reduction potential in this case was not determined for the biruthenium(II) bpbimH_2 compounds. The second Ru(II) ion on the remote coordination site of the bridging ligand, in general, enhances its electron-accepting ability (shifts its reduction potential to less negative) due to the 2+ charge, provided that the π^* orbitals of two coordination sites interact substantially. However, since diprotonation (2+) on the remote coordination site of bpbimH_2 of Ru(bpy)₂(bpbimH_2)²⁺ gives no energy shift for the phosphorescence,²⁸ a significant low-energy shift of the reduction potential in the bimetallic compounds is hardly expected. As for the oxidation potentials, $E_{1/2}(\text{Ru(III)}/\text{Ru(II)})$, the peak shift of the differential-pulse voltammogram was indiscernible with the coordination of the second metal ion.

A matrix element between d_x electrons on Ru(II) and Ru(III) ($H_{\text{II III}}$) in a mixed-valence compound can be experimentally assessed. The matrix element ($H_{\text{II III}}$) for a mixed-valence compound, Ru(bpy)₂(bpbimH_2)Ru(bpy)₂⁵⁺, was found to be very small (8–10 meV) from the intensity of the intervalence transition.^{12b} Stabilization energy of the Ru(III) state due to Ru(II)–Ru(III) electronic exchange interaction is estimated to be very small ($H_{\text{II III}}^2/\Delta E \sim 0.1 \text{ meV}$) by assuming a two-state model from the matrix element and the intervalence transition energy (ΔE).^{29–31} Formation of Ru(III) in the biruthenium(II) compound, which is stabilized by several mechanisms including the electronic exchange interaction, is expected to split the oxidation potentials of the equivalent Ru(II) ions.³⁰ The insignificant broadening of the oxidation differential-pulse voltammogram of [Ru(bpy)₂]₂(bpbimH_2)⁴⁺ implies that the splitting of the oxidation potential is smaller than 40 mV.³¹ Similarly, the formation of Ru(III) in the excited CT state may bring about a so small low-energy shift of phosphorescence as observed.

Slower energy transfers from the excited biruthenium(II) compounds to anthracene compared to that for monoruthenium(II) (Table II) are in accord with the weak Ru–Ru interaction. This is because the low efficiency of the collisional intermolecular energy transfer demonstrates incomplete delocalization of CT excitation through the two metal sites in the lifetime ($<10^{-10} \text{ s}$) of the collisional complex. Energy transfer in a dimetallic compound was exploited to determine the energy-transfer rate, where Ru-to-phen CT is higher than Ru-to-dmbpy CT by 80 meV as Table I shows. Since the TA acquired just after the laser excitation of Ru(dmbpy)₂(bpbimH_2)Ru(phen)₂⁴⁺ was the same as that of Ru(dmbpy)₂(bpbimH_2)²⁺, the energy transfer must occur within 50 ns at ambient temperature. Therefore, the rate of excitation hopping between the two metal sites is in a range of $2 \times 10^7\text{--}10^{10}$

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s^{-1} , demonstrating a weak Ru-Ru interaction between the ruthenium(II) ions.

Less than 50% of the Ru(II) sites were excited to the phosphorescent state of the biruthenium(II) compound, $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$, as is shown in Figure 9. The laser intensity was large enough to convert the majority of the mononuclear compounds to the excited state. The low excitation efficiency of the biruthenium compounds, therefore, implies that the excitation of both of Ru(II) ions in the biruthenium compounds leads to annihilation of excited states.

The annihilation of the excited Ru(II) ions can be initiated by electron transfer to form a Ru(III) ion and a reduced bpy which are separated by the bridging ligand. The rapid back-electron-transfer may prevent detection ($>10^7 \text{ s}^{-1}$). This speculation is more probable because intramolecular electron transfer in a mixed-metal (Ru(III) and Rh(II)) compound, $(\text{bpy})_2\text{Ru}(\text{bpimH}_2)\text{Rh}(\text{bpy})^{5+}$, was too fast to be detected by means of picosecond laser photolysis.²⁸ The electron transfer as the initial process of the annihilation is allowed from an energetic point of

view. That is, the ergonicity of electron transfer is calculated to be $-(2 \times 2.0 - 0.83 - 1.71) \text{ eV}$ from the excitation energy and the redox potentials. Annihilation of excited states was postulated to occur between $\text{Cr}(\text{CN})_6^{3-}$ moieties linked by $\text{Ru}(\text{bpy})_2^{2+}$.³²

Registry No. bpimH, 1137-68-4; dpbime, 102948-77-6; $\text{Ru}(\text{pbimH})_3^{2+}$, 80634-41-9; $\text{Ru}(\text{bpy})_2(\text{dpbime})^{2+}$, 137744-52-6; $\text{Ru}(\text{bpy})_2(\text{bpimH}_2)^{2+}$, 137729-41-0; $\text{Ru}(\text{dmpby})_2(\text{bpimH}_2)^{2+}$, 137744-53-7; $\text{Ru}(\text{phen})_2(\text{bpimH}_2)^{2+}$, 137744-54-8; $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$, 137744-55-9; $[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{4+}$, 137744-56-0; $[\text{Ru}(\text{dmpby})_2]_2(\text{bpimH}_2)^{4+}$, 137744-57-1; $\text{Ru}(\text{dmpby})_2(\text{bpimH}_2)\text{Ru}(\text{phen})_2^{4+}$, 137744-58-2; $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $\text{Ru}(\text{dmpby})_3^{2+}$, 32881-03-1; $\text{Ru}(\text{phen})_3^{2+}$, 22873-66-1; $[\text{Ru}(\text{bpy})_2]_2(\text{bpimH}_2)^{2+}$, 137744-59-3; $[\text{Ru}(\text{pbimH})_3](\text{ClO}_4)_2$, 80634-42-0; $[\text{Ru}(\text{bpy})_2(\text{dpbime})](\text{ClO}_4)_2$, 137744-61-7; $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})(\text{ClO}_4)_2$, 137744-62-8; RuCl_3 , 10049-08-8; NaClO_4 , 7601-89-0; *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$, 19542-80-4; HClO_4 , 7601-90-3; CF_3COOH , 76-05-1; glycerol, 56-81-5; anthracene, 120-12-7.

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Electronic Absorption Spectra of the Iron(II) Complexes of 2,2'-Bipyridine, 2,2'-Bipyrimidine, 1,10-Phenanthroline, and 2,2':6',2''-Terpyridine and Their Reduction Products

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The iron(II) complexes $[\text{Fe}(\text{bpy})_3]^{2+}$ (I), $[\text{Fe}(\text{bpym})_3]^{2+}$ (II), $[\text{Fe}(\text{phen})_3]^{2+}$ (III), and $[\text{Fe}(\text{terpy})_2]^{2+}$ (IV) (bpy, 2,2'-bipyridine; bpym, 2,2'-bipyrimidine; phen, 1,10-phenanthroline; terpy, 2,2':6',2''-terpyridine) were subjected to two (for IV) or three (for I-III) stepwise one-electron electrochemical reductions; the products were studied in situ by solution UV-vis-near-IR spectroscopy. Bands of the reduced species in the UV-vis-near-IR region were observed and assigned to anion radical ligands. The reductions took place in all cases on individual ligands, the spectra of IV^- as well as IV^{2-} showing equivalent features similar to those of $[\text{Li}^+[\text{terpy}]^-]$.

Introduction

Polydentate ligands containing N-donor heterocyclic rings have played an important role in the development of coordination chemistry and continue to be of widespread interest, particularly centered upon complexes of diimine-type ligands,¹ such as 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpym), 1,10-phenanthroline (phen), and 2,2':6',2''-terpyridine (terpy). Although the coordination chemistry of phen and bpym, as well as terpy is well studied,^{1d-k} there have been few spectroelectrochemical studies of these metal complexes.^{1e,2} A preliminary account of our results for III has appeared^{1b} (we have ourselves published such studies for Kaim's³ μ -bpym complexes, while Berger and McMillin^{2c} have independently investigated $[\text{Ru}(\text{terpy})_2]^{2+}$). In this paper we describe spectroscopic results for I-IV and their reduced species.

Experimental Section

Materials. Spectrol grade dimethylformamide (DMF) was purchased from BDH and stored over molecular sieves. α -Diimine ligands were used as received from Aldrich (2,2'-bipyridine and anhydrous 1,10-phenanthroline) or Lancaster Synthesis (2,2'-bipyrimidine). 2,2':6',2''-Terpyridine was prepared by literature methods.^{1j} Tetra-*n*-butylammonium tetrafluoroborate ($\text{TBA}(\text{BF}_4)$) as a supporting electrolyte was prepared by metathesis of tetra-*n*-butylammonium hydroxide and HBF_4 in water, washed repeatedly with water, and purified by successive recrystallizations from ethyl acetate/pentane followed by drying in vacuo at 80 °C. Microanalyses were performed in the Microanalysis Lab, University of Glasgow, Scotland, for Fe(II) complexes. The complexes were prepared as well-formed crystalline materials by reaction between ferrous sulfate and the appropriate ligand in a 1:3 mole ratio (1:2 mole

ratio for IV) in aqueous solution^{1f,4} and precipitated by addition of ammonium tetrafluoroborate (under these conditions, II is known^{1f} to precipitate with seven molecules of water per formula unit, while the other salts prepared are known to be anhydrous^{1j,4b}). $[\text{Li}^+[\text{terpy}]^-]$ was synthesized by direct reaction between lithium metal and terpy in ether at room temperature using an ultrasonic bath.

Instrumentation. Cyclic voltammetric and spectroelectrochemical experiments were performed in DMF (Metrohm cell for cyclic voltam-

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