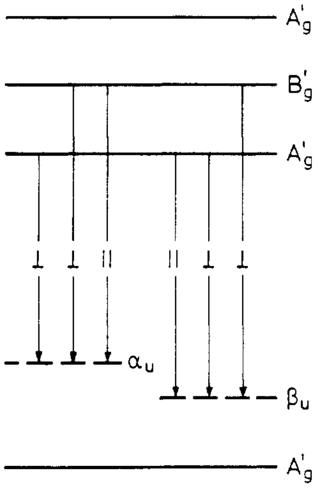

Figure 6. Energy level diagram for the electronic states of a β chain in a single crystal of $[Pt(bpm)(CN)_2]$.

in Figure 6. Electric dipole transitions between the ground state and these excited states are parity forbidden. By vibronic coupling with excited states of odd parity, the following polarized optical transitions $A_g' \leftrightarrow A_g'$, B_g' with vibrations of symmetry α_u and β_u are expected (cf. also Figure 6):

	A_g'	B_g'
A_g'	α_u:E∥y	α_u:E∥x or z
	β_u:E∥x or z	β_u:E∥y

The very weak absorption at $\bar{\nu} \sim 21\,000$ cm^{-1} can be assigned to a spin- and symmetry-forbidden transition from the ground electronic state A_g' to the triplet components of ^3B_g parentage.

The broad emission band X is due to the radiative deactivation of the lowest excited triplet components. Both the polarization properties of band X and its dependence on temperature and applied magnetic fields can be understood on the basis of the energy level scheme given in Figure 6. The energy order of the lowest excited electronic states and of the vibrational quanta have been chosen according to the experimental results, as will be shown below. The energy distance between the triplet components is expected to be on the order of several wavenumbers.

At $T = 1.9$ K only the lowest excited state A_g' is appreciably occupied. The vibronic transition $A_g' \rightarrow A_g' + \beta_u$ yields both an E∥x and an E⊥x emission, both of equal energy. These emissions correspond to the nonpolarized shoulder of band X at $\bar{\nu} \sim 19\,600$ cm^{-1}, whereas the transition $A_g' \rightarrow A_g' + \alpha_u$ is hidden below the vibrational structure at $\bar{\nu} < 19\,600$ cm^{-1}. With increasing temperature the state B_g' becomes thermally populated. The vibronic transition $B_g' \rightarrow A_g' + \beta_u$ is E⊥x polarized. It is composed of an E∥**a** and a more intense E⊥**a** component. Because of the admixture of the singlet $B_g'(^1B_g)$ to the triplet B_g' via spin-orbit coupling, the radiative deactivation rate for the transition $B_g' \rightarrow A_g' + \beta_u$ will be distinctly larger than that for the corresponding transition from the lowest excited state A_g'. That explains the temperature-induced increase of the emission intensity at $\bar{\nu} \sim 19\,600$ cm^{-1}. The small energy difference between A_g' and B_g' cannot be detected spectroscopically. The radiative rate of the process $B_g' \rightarrow A_g' + \alpha_u$ is obviously lower than that of the transition $B_g' \rightarrow A_g' + \beta_u$.

The β-chain emission can be influenced by homogeneous magnetic fields with **H**⊥**x** but not with **H**∥**x**. Fields with **H**∥**x** do not change the symmetry of the system. For the orientation **H**⊥**x**, however, the symmetry is reduced to C_i, and the states $A_g'(A_g')$ and $A_g'(B_g')$ can mix. As a consequence, the $A_g'(B_g')$ component of the lowest excited electronic state raises the radiative rate at low temperatures and an effect similar to that found with a temperature increase results. The slow intensity increase of the X band for **H**∥**a** is due to the effective **H**⊥**x** component.

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Supplementary Material Available: Tables of positional parameters and bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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Photophysics and Photoredox Reactions of Ligand-Bridged Binuclear Polypyridyl Complexes of Ruthenium(II) and of Their Monomeric Analogues

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The influence of bridging ligand (BL), spectator ligand (LL), and solvent on the photophysical properties of the MLCT state has been assessed in a series of mono- and binuclear polypyridyl complexes of Ru(II); $\{[(LL)_2Ru]_n(BL)\}^{2n+}$ (n = 1, 2; BL = 2,2'-bipyrimidine (bpym), 2,3-bis(2-pyridyl)pyrazine (dpp); LL = a substituted 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen)). A comparative study of the two series of complexes with dpp or bpym as the bridging ligand allows some of the reported anomalies in the behavior of the latter series of complexes to be explained. Features in the excited-state absorption spectra of the ligand-bridged binuclear complexes are also reported. Chemical and photochemical oxidation of the binuclear complexes from the (II,II) state to (II,III) and (III,III) states are examined. Complexes in the (III,III) state are unstable and rapidly cleave into monomeric components.

Introduction

Extensive photophysical and photochemical studies on the polypyridyl complexes of Ru(II) in the last 2 decades[1,2] have allowed development of quantitative descriptions of the excited-state dynamics and also practical applications of these complexes in areas such as photochemical conversion of solar energy. With the enormous success obtained with the mononuclear complexes, increasing attention is being focussed on polynuclear ("supramolecular") complexes.[3-7] Optical excitation of polynu-

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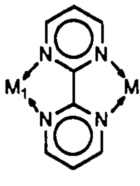
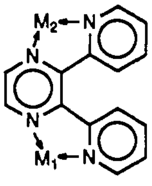
clear complexes provide an elegant means of studying phenomena such as extended long-range interactions between the molecular components, mixed-valence compounds, and multielectron-transfer processes. The success and confidence allow for intelligent design of "tailored photocatalysts" for various practical applications.

Multidentate ligands such as 2,2′-bipyrimidine (bpym) or 2,3-bis(2-pyridyl)pyrazine (dpp) serve as templates for generating polynuclear polypyridyl complexes of the type $[(LL)_2M]_n(BL)^{2n+}$. Very recently, a few encouraging reports have appeared, describing the synthesis and photochemical properties of such polypyridyl–ruthenium complexes with different bridging ligands (BL), e.g., 2,2′-bipyrimidine (bpym),[8–10a,13] 2,3-bis(2-pyridyl)pyrazine (dpp),[11a] 2,3-bis(2-pyridyl)quinoxaline (dpq),[10a,b] 4′,4′-phenanthrolino-5′,6′:5,5-pyrazine (ppz),[12] 4,4′-bipyridine (4,4′-bpy),[13–15] *m*-dipyrazino[2,3-*f*][2′,3′-*h*]quinoxaline (HAT),[16] 2,2′,3,3′-tetrakis(2-pyridyl)-6,6′-biquinoxaline (tpbq),[10a,17] *trans*-1,2-bis(4-pyridyl)ethane (bpa),[14a,b,15] and 3,5-bis(2-pyridyl)triazole (dpt).[18a,b] We will refer to the non-bridging ligands associated with the two metal centers as "spectator ligands". Homo- and heterobinuclear complexes containing identical or different spectator ligands have been characterized. Depending on the nature of the bridging ligand, the interactions between the metal centers have been found to be strong or weak (see refs 8–18 and 19–21 for some recent examples of strong and weak coupling cases, respectively). The limited data available on a few of these complexes allow for some generalizations to be made, but these data are far from offering a thorough understanding. For example, the relationship between the interaction of the metal centers through the bridging ligand and the observed photophysical properties is not well established.

Knowledge of the luminescence and redox properties, ways of tuning them, and study of the excited-state absorption spectra are imperative for a proper understanding of the photophysics and in the development of their photochemistry. Towards this goal, we synthesized several ligand-bridged polypyridyl complexes of Ru. Investigations have been made on the photophysics and photoredox chemistry of the bimetallic complexes with the aid of conventional spectroscopic techniques and nanosecond laser flash photolysis. Herein we present our observations on complexes of the type $\{[(LL)_2Ru]_n(BL)\}^{2n+}$ (n = 1, 2; BL = 2,2′-bipyrimidine (bpym) and 2,3-bis(2-pyridyl)pyrazine (dpp); LL = 2,2′-bipyridine (bpy), 4,4′-dicarboxy-2,2′-bipyridine (4,4′-dcbpy), 1,10-phenanthroline (phen) or 5-chloro-1,10-phenanthroline (5-Cl-phen) in solution at room temperature and also in low-temperature glasses. A few exploratory studies on the representative members of this class of compounds with normal 2,2′-bipyridine as the spectator ligand ($\{[(bpy)_2Ru]_n(BL)\}^{2n+}$) are available.[8–13,22–24] Our motivations for further examination of this class of complexes are 3-fold: (a) to examine the "tunability" of the photophysical properties via a quantitative examination of a selected series of complexes, (b) to compare the properties of the two series of the complexes in order to identify the origin of the wide differences and inconsistencies in the reported behavior of these two series of complexes, and, more importantly, (c) to explore thermal and photochemical redox processes of the binuclear complexes in solution. Data on the influence of the bridging ligand (BL), spectator ligand (LL), and solvent on the photophysics and the absorption spectra of the MLCT excited state(s) are presented. Chemical and photochemical oxidations of the complexes from the (II,II) state to the mixed-valence (II,III) and (III,III) species are also examined. It is shown that the complexes in the (III,III) state are unstable and rapidly cleave to their monomeric components. There have also been several reports describing properties of bimetallic complexes of dpp and bpym and cyano,[11b] ammine,[11c] or carbonyl groups[11d] as spectator ligands.



bpym complex



dpp complex

Experimental Section

Materials. Polypyridyl ligands 2,2′-bipyrimidine (bpym) (Ventron), 2,3-bis(2-pyridyl)pyrazine (dpp) (Aldrich), 2,2′-bipyridine (bpy) (Alfa), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) (Alfa), 1,10-phenanthroline (phen) (Alfa), 5-chloro-1,10-phenanthroline (5-Cl-phen) (GF Smith), and 2,2′-bipyridine-4,4′-dicarboxylic acid (4,4′-dcbpyH_2) (Alfa) were all commercial samples and were used as supplied. *cis*-$[Ru(bpy)_2Cl_2]$ was a commercial sample from Strem and was recrystallized in dark before use. Water was distilled twice on a quartz still before use. All other chemicals and solvents were reagent grade and were used without further purification.

The binuclear complexes $[(LL)_2Ru]_2(BL)^{4+}$ were prepared by a slightly modified form of earlier reported synthetic procedures.[13,17] Sequential chelation $Ru(LL)_2Cl_2 \rightarrow [Ru(LL)_2(BL)]^{2+} \rightarrow [Ru(LL)_2]_2(BL)^{4+}$ was carried out with use of at least a 2-fold excess of BL in the first step and subsequent control of purity at each step so as to prevent formation of luminescent side-products. As has been noted recently by Meyer et al.,[13] we have found this procedure of sequential chelation gives higher yields of the desired mono- or binuclear complex without formation of the higher/oligo nuclear complexes. The typical synthetic procedure used is as follows.

(i) Synthesis of $[Ru(LL)_2Cl_2]$, LL = Me_2bpy, 4,4′-dcbpyH_2, phen, and 5-Cl-phen. These complexes were prepared by reacting stoichiometric quantities of $RuCl_3 \cdot xH_2O$ and the ligand LL in DMF as described earlier.[10] Even when the purified product samples gave satisfactory ele-

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mental analyses, the purity of these complexes as well as that of $[Ru(bpy)_2Cl_2$ was further controlled using luminescence as a probe. The highly luminescent tris chelate $Ru(LL)_3^{2+}$ was often found to be present in trace quantities and was removed by column chromatography (neutral alumina using acetonitrile as eluent). Column fractions that are devoid of the tris-chelate emission were collected separately, and the bis(polypyridyl) complex recovered from these fractions alone were used for further chelation with the bridging ligand BL.

(ii) Synthesis of Mononuclear Complexes $[Ru(LL)_2(BL)]^{2+}$, e.g., $Ru(Me_2bpy)_2(dpp)^{2+}$. A 0.30-g (0.556-mmol) sample of *cis*-$Ru(Me_2bpy)_2Cl_2$ was dissolved in 30 mL of DMF under Ar in the dark (to avoid possible cis–trans isomerization) and was added to 0.325 g (1.38 mmol) of dpp. The solution was heated under reflux under Ar with continuous stirring of the solution. After 4 h (15 h for the corresponding 4,4′-dcbpy complex), the reaction mixture was allowed to cool and solvent removed on a rotary evaporator. The resulting solid was dissolved in 10 mL of H_2O and filtered in order to remove excess free ligand BL. To the filtrate was added 1–2 g of NH_4PF_6 in 10 mL of H_2O, and the mixture was placed in a refrigerator overnight. The resulted precipitate was isolated by suction filtration and washed well with water, with a 3:7 ethanol–diethyl ether mixture, and finally with diethyl ether. The solid was air-dried in vacuo (yield >80%). The complex was purified on a neutral alumina column (5 cm × 15 cm), which was packed and eluted with acetonitrile. Satisfactory analytical results were obtained for all of the complexes.

(iii) Synthesis of Binuclear Complexes $[Ru(LL)_2]_2(BL)^{4+}$. (a) $[(Me_2bpy)_2Ru]_2(dpp)^{4+}$. A 0.75-g (1.39-mmol) sample of $Ru(Me_2bpy)_2Cl_2$ was dissolved in 50 mL of DMF under Ar and was added to 0.39 g (0.556 mmol) of $Ru(Me_2bpy)_2(dpp)^{2+}$. The resulting solution was heated at reflux for 4 h with continuous stirring. The solution was allowed to cool, solvent was removed on a rotovap, and the complex was precipitated as the hexafluorophosphate salt by using a saturated solution of ammonium hexafluorophosphate, filtered, washed with ether, and air-dried. The binuclear complex was subsequently purified on a neutral alumina column (5 cm × 15 cm), which was packed and eluted with acetonitrile. Purple mononuclear complex elutes first, followed by the binuclear complex (the binuclear complex of dpp is pink and that of bpym is green). Satisfactory analytical results were obtained for all the complexes. The tetracationic complex $[Ru(4,4'\text{-dcbpyH}_2)_2]_2(dpp)(PF_6)_4$ was also prepared by the same procedure.

(b) $[(4,4'\text{-dcbpyH})_2Ru]_2(dpp)$. A 0.10-g (0.121-mmol) sample of $Ru(4,4'\text{-dcbpyH}_2)_2(dpp)^{2+}$ was dissolved in 30 mL of H_2O at pH 9.00 under Ar and was added to 0.083 g (0.123 mmol) of *cis*-$Ru(4,4'\text{-dcbpy})_2(H_2O)_2$. The resulting solution was heated at reflux in the dark, under continuous stirring. After 36 h, the solution was allowed to cool. Lowering of the pH of the solution to 2.5 resulted in the precipitation of a dark violet solid. The mixture was transferred to a refrigerator overnight, after which the solid was collected by suction filtration. The solid was washed with water (pH 3.00) followed by acetone–ether mixture and dried in vacuo for 40 min. Yield: 85%. The isolated Ru complex, though insoluble in most of the organic solvents, dissolves readily in dilute alkaline or acidic aqueous solutions.

During purification and in later studies, it was noted that the binuclear complexes were unstable in alcoholic solvents and decomposed with time. The decomposition was more rapid and severe with bpym as a bridging ligand than with dpp. Hence data on these complexes in alcohols reported in this work are to be considered as approximate indicators only.

Methods. Excited-state absorption and luminescence decay studies were made on a nanosecond laser flash photolysis set up by using 15 ns, 532 nm pulses from a Q-switched Nd YAG (oscillator)/Nd glass (amplifier) laser.

Steady-state photolysis studies were carried out by using a 150-W quartz halogen lamp, fitted with 5-cm water (IR) and 495-nm cutoff Corning glass filters.

Luminescence spectra and quantum yield studies were made on either a Perkin-Elmer MPF 4F or a Spex Flurolog-2 spectrofluorimeter, both equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. In numerous cases, both uncorrected and corrected emission maxima are quoted. Corrected emission maxima reported in this work are believed to be accurate up to ca. 820 nm. Quantum yields were made relative to $Ru(bpy)_3^{2+}$ in water as a reference ($\phi = 0.042$)[1] and are corrected for variations in the light source, detector response, and solvent refractive index. Experimental errors in the reported data are emission maxima ±3 [illegible] emission lifetimes ±10%, quantum yield ±20%, and redox po- [illegible] V. Emission lifetimes reported in this work are for de- [illegible] ns.

Results and Discussion

This study consists essentially of two parts: (i) a detailed investigation (reexamination?) of factors that control the excited state photophysics in ligand-bridged binuclear complexes of Ru and (ii) an exploratory photochemical study of photoredox reactions of these systems. Results of the photophysical studies are discussed first, followed by those of chemical and photochemical oxidations. As noted in the Experimental Section, long-term stability of the binuclear complexes in different organic solvents was rather limited, especially in alcohols. Bipyrimidine complexes in general are much less stable than the dpp analogues.

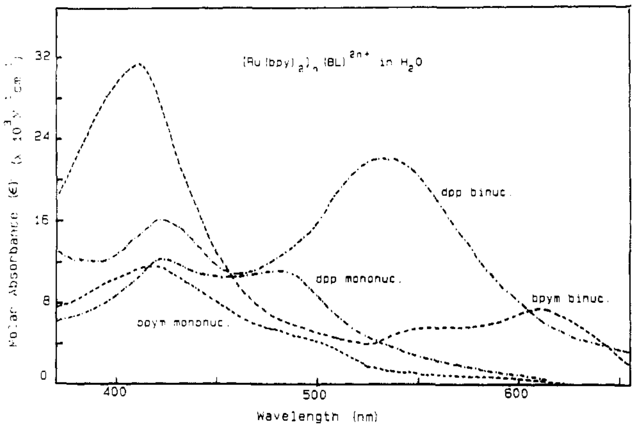


Figure 1. Comparison of the ground-state absorption spectra of mono- and binuclear complexes $[Ru(bpy)_2]_n(BL)^{2n+}$ ($n = 1, 2$; BL = dpp, bpym) in aqueous solution.

I. Photophysics of Ligand-Bridged Binuclear Polypyridyl Complexes and of Their Mononuclear Analogues. It was mentioned in the introductory paragraphs that the principal focus of this study is to examine the influence of the spectator and bridging ligands on the MLCT excited-state photophysics. For this purpose, a series of Ru complexes of dpp with different spectator ligands were synthesized and their properties determined. Absorption and luminescence properties of several ligand-bridged binuclear Ru complexes and their mononuclear analogues were determined in different solvents. There have been a few reports[8-13,22-24] on the synthesis and characterization of the MLCT excited state of the parent member of these complexes ($\{[(bpy)_2Ru]_n(BL)\}^{2n+}$).

Table I presents data on the absorption properties of the mono- and binuclear Ru complexes involving dpp: $[(LL)_2Ru]_n(dpp)^{2n+}$ ($n = 1, 2$; LL = either a substituted 2,2′-bipyridine or 1,10-phenanthroline (phen) determined in this work). Table II presents analogous absorption spectral data for the bpym complexes. A word of explanation is in order on the presentation of absorption spectral data in Tables I and II. We prefer to list relative intensities of various bands with ε values for the normalized reference band. On the basis of our own experience and from a comparison of literature data for numerous polypyridyl complexes and metalloporphyrins, the relative intensity of the absorption bands are more accurately reproduced in various labs than the absolute ε values.

Figure 1 presents a comparison of the absorption spectra of the mono- and binuclear Ru(II) complexes $\{[(bpy)_2Ru]_n(BL)\}^{2n+}$ (BL = dpp, bpym, $n = 1, 2$) in aqueous solution. The absorption spectra of the dpp and bpym complexes consist in general of two maxima in the visible wavelength region. The high-energy band located at 420–430 nm is rather insensitive to the nature of the ligand BL and presence of one or two metal centers coordinated to BL and is assigned as due to M–LL charge transfer (CT). The low-energy band due to M–BL CT is located in the 460–490-nm region in the mononuclear complexes. Examination of the relative intensities of the two charge-transfer bands of interest shows that, in the mono- and binuclear complexes of dpp, M–LL and M–BL bands have comparable intensities. The absolute intensities of the M–LL band are comparable in the mononuclear complexes with dpp or bpym ($\epsilon \approx 11\,000$ M^{-1} cm^{-1}).

In the bpym complexes, the M–BL band appears weak—as a shoulder with about half the intensity in the monomer and one-quarter of the intensity in the binuclear complexes, both relative to their respective M–LL band. In both binuclear complexes, the

Table I. Absorption and Spectral Properties of Mono- and Binuclear dpp Complexes of the Type $[Ru(LL)_2]_n(dpp)]^{2n+}$ in Solution at Room Temperature

LL	solvent	abs max, nm (rel intens)			ϵ(M-LL), mol^{-1} cm^{-1}
		M-BL	M-LL	π-π^*(LL/BL)	
Mixed-Ligand Complexes $[Ru(LL)_2(dpp)]^{2+}$					
Me_2bpy	CH_2Cl_2	471 (0.99)	445 (1.00)	285 (4.71)	
	CH_3CN	474 (0.98)	436 (1.00)	284 (5.64)	10 900
	H_2O	486 (1.00)	424 (1.00)	282 (5.73)	
bpy	CH_2Cl_2	465 sh (0.92))	440 (1.00)	285 (6.60)	
	CH_3CN	468 sh (0.96)	434 (1.00)	284 (5.79)	11 500
	EtOH	466 sh (0.91)	430 (1.00)		
	CH_3OH	470 (0.93)	432 (1.00)	284 (5.90)	
	H_2O	476 (0.96)	424 (1.00)	282 (6.20)	12 000
phen	CH_2Cl_2	460 (0.99)	445 (1.00)	263 (4.91)	
	CH_3CN	463 (1.00)	435 (1.00)	261 (7.00)	10 400
	H_2O	472 (1.08)	430 (1.00)	262 (6.08)	
5-Cl-phen	CH_2Cl_2	462 (1.02)	447 (1.00)	265	13 500
	CH_3CN	462 (1.04)	430 (1.00)	265 (7.41)	
	H_2O	466 (0.99)	428 (1.00)	266 (6.14)	
4,4'-$dcbpy^{2-}$	H_2O (pH 7)	461 (1.00)	438 sh (1.00)	298 (3.51)	
4,4'-$dcbpyH_2$	H_2O (pH 0)	462 (1.00)	438 sh (1.00)	305 (3.26)	
	CH_3OH	458 (1.00)	432 (1.00)		
dpp	CH_3CN	457 (1.00)	430 sh (0.83)	294	13 750
	CH_3OH	452 (1.00)	430 sh (0.82)	292	
	H_2O	458 (1.00)	430 sh (0.81)	297 (3.11)	13 300
Binuclear Complexes $[Ru(LL)_2]_2(dpp)^{4+}$					
bpy	CH_2Cl_2	519 (1.21)	427 (1.00)	284 (5.70)	
	CH_3CN	526 (1.25)	425 (1.00)	284 (5.79)	19 800
	EtOH	522 (1.18)	424 (1.00)	282 (5.68)	
	CH_3OH	525 (1.28)	424 (1.00)	283 (5.93)	
	H_2O	530 (1.39)	421 (1.00)	284 (5.87)	17 000
phen	CH_3CN	526 (1.12)	424 (1.00)		20 800
4,4'-$dcbpy^{2-}$	H_2O (pH 7)	530 (1.05)	438 (1.00)	298 (3.86)	
4,4'-$dcbpyH_2$	H_2O (pH 0)	518 (0.84)	448 (1.00)	306 (3.17)	
	CH_3OH	530	430 (1.00)		

Table II. Absorption and Spectral Properties of Mono- and Binuclear bpym Complexes of the Type $[Ru(bpy)_2]_n(bpym)]^{2n+}$ in Solution at Room Temperature

LL	solvent	abs max, nm (rel intens)			ϵ(M-LL), mol^{-1} cm^{-1}
		M-BL	M-LL	π-π^*(LL/BL)	
Mixed-Ligand Complexes $[Ru(LL)_2(bpym)]^{2+}$					
bpy	CH_2Cl_2	480 sh (0.48)	420 (1.00)	287 (4.88), 244	10 500
	CH_3CN	480 sh (0.48)	422 (1.00)	284 (4.92), 244 (3.28)	
	EtOH	480 sh (0.46)	420 (1.00)	284 (4.34), 242 (3.04)	
	CH_3OH	480 sh (0.47)	420 (1.00)	284 (4.95), 242 (4.22)	
	H_2O	480 sh (0.43)	418 (1.00)	282 (4.54), 240 (2.11)	11 300
bpym	CH_3CN	454 (1.05)	412 (1.00)		8 600
	H_2O	452 (1.03)	412 (1.00)		
Binuclear Complexes $[Ru(LL)_2]_2(bpym)^{4+}$					
bpy	CH_2Cl_2	588 (0.24), 540 (0.19)	412 (1.00)	282 (3.71)	
	CH_3CN	594 (0.23), 540 (0.18)	412 (1.00)		29 800
	H_2O	608 (0.22), 556 (0.17)	408 (1.00)	279 (3.31)	31 300

magnitudes of ϵ values for the M-BL and M-LL bands suggest that the total integrated absorption under the broad MLCT absorption remains the same. However, there is some redistribution of intensities between the M-BL and M-LL bands. For example, in the parent binuclear complexes with 2,2'-bpy as the spectator ligand, the ϵ values for the M-LL and M-BL bands are $\approx$31 000 and $\approx$6900 M^{-1} cm^{-1} with bpym as the bridging ligand vs $\approx$20000 and $\approx$24 000 M^{-1} cm^{-1} for the corresponding bands in the dpp complex. (Given the broad absorption features of the charge-transfer bands in solution at room temperature as compared to observed peak separation between M-BL and M-LL, some overlap of these bands is bound to occur. Hence, the above comparison of crude band intensities is to be taken qualitatively!) In all of the complexes, intraligand π-π^* absorptions are located at 297 (dpp), 282 (bpy), and 262 (phen) nm.

The absorption spectral features of ligand-bridged binuclear complexes and of their monomeric analogues have been the subject of discussion recently.[8-13,22-24] While we tend to agree with the reported observations on the dpp complexes, we find the data reported for the "bpym" complexes are either incomplete or inaccurate. It has been reported[9,10a,11,12] that the complexes are "anomalous" with the absence of typical M-BL charge-transfer bands in the monomers and lack of room-temperature luminescence in the binuclear complexes. The mononuclear bpym complexes do have their M-BL bands appearing as a shoulder at ca. 475-480 nm.

Charge-transfer states in general are known to be solvent sensitive, and the absorption spectral shifts with solvent polarity listed in Table I and II confirm MLCT assignment of the absorption bands in the visible-wavelength region of these complexes. With increasing solvent polarity, the broad MLCT absorption splits into two distinct bands. The low-energy M-BL band red shifts while the higher energy M-LL band blue shifts. Similar but smaller magnitude effects are observed in the binuclear complexes. Thus the M-BL and M-LL bands are well separated by over 50 nm in water but the separation is $\leq$20 nm in a nonpolar solvent such as CH_2Cl_2. The effects are again more pronounced in "dpp" complexes.

There are several factors that can be responsible for the observed solvent effects in the mononuclear complexes: (a) dipolar character of the charge-transfer state, (b) H-bonding interactions of the lone pair on the pyrazyl and pyridyl N centers of the bridging ligand

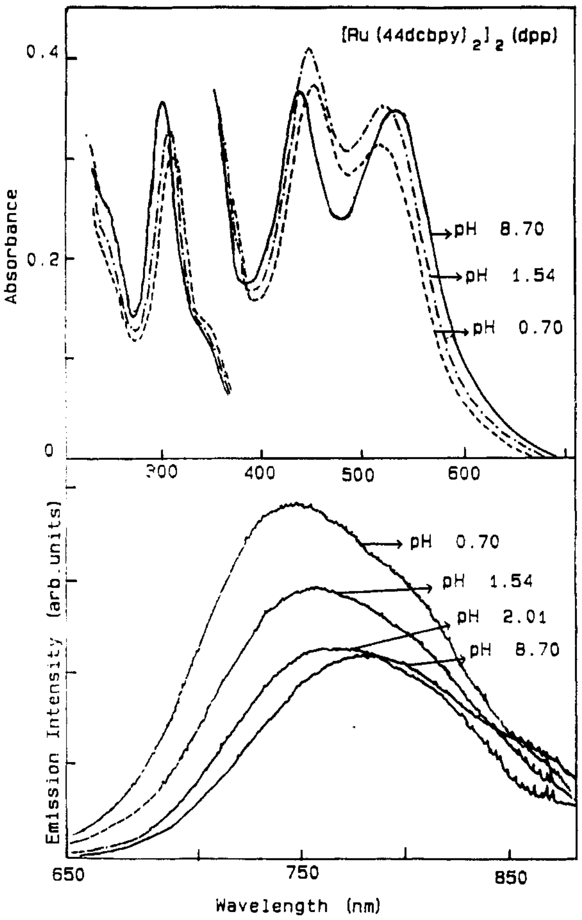
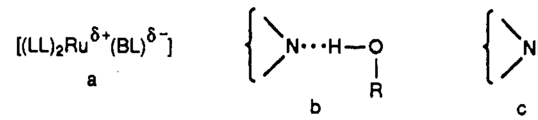


Figure 2. Top: Absorption spectra of $[Ru(4,4'\text{-}dcbpy)_2]_2(dpp)$ in aqueous solution at three different pH values: 8.70, 1.54 and 0.70. Bottom: Luminescence spectra of $[Ru(4,4'\text{-}dcbpy)_2]_2(dpp)$ in aqueous solution at four different pH values: 8.70, 2.01, 1.54, and 0.70.

with solvents such as alcohol, and (c) protonation effects at the imino nitrogens. Marginal spectral shifts with solvent observed



with binuclear complexes suggest that the influence of the dipolar character (type a) is negligible. The extra nitrogen centers can undergo protonation, and when this occurs, the absorption band corresponding to M–BL CT does red shift considerably, leaving the M–LL band unaffected. The mononuclear dpp and bpym complexes, however, are weak bases, exhibiting protonation behavior only in concentrated acid solutions: $pK_a = -2.9$ and -3.8 for $Ru(bpy)_2(bpym)^{2+}$ and $Ru(bpy)_2(dpp)^{2+}$, respectively.[25] Hence, it is likely that the dominant factor is the H-bonding interaction.

dpp Complexes with Ionizable 4,4'-Dicarboxy-2,2'-bipyridine (4,4'-dcbpy) Ligands, $[Ru(4,4'\text{-}dcbpy)_2]_n(dpp)^{n+}$. The dpp complexes with ionizable 4,4'-dicarboxy-2,2'-bipyridine (4,4'-dcbpy) as spectator ligands, $[Ru(4,4'\text{-}dcbpy)_2]_n(dpp)$ ($n = 1, 2$), examined in this work form an interesting class of compounds complimentary to those with normal "bpy" ligands. In aqueous solution, the absorption spectra of these complexes are pH dependent. Figure 2 (top) presents some representative absorption spectra of this binuclear complex as three different pH values. For reasons elaborated below (known protonation behavior of the chelated dpp and dcbpy ligands, precipitation/dissolution in aqueous soluion at different pH values and characterization of the resulting complexes, and conductivity), the absorption spectral shifts with pH are attributed to possible protonation of the peripheral carboxy group substituents of the spectator bpy ligand.

The absorption spectrum is pH independent at pH ≥5.0, suggesting the existence of fully deprotonated dcbpy groups under these conditions. The complexes are hence overall anionic in neutral or alkaline solutions and cationic in acidic solutions: at pH ≥6, as $[Ru(4,4'\text{-}dcbpy)_2](dpp)^{2-}$ and $[Ru(4,4'\text{-}dcbpy)_2]_2(dpp)^{4-}$; at pH ≈0, as $[Ru(4,4'\text{-}dcbpyH_2)_2](dpp)^{2+}$ and $[Ru(4,4'\text{-}dcbpyH_2)_2]_2(dpp)^{4+}$. At intermediate pH values, partial protonation of the 4,4'-dcbpy ligand occurs, resulting in the existence of complexes that are either cationic, anionic, or neutral. The isoelectric points of these complexes are found in the narrow range of pH 2.3–2.5 where precipitation of the neutral complex occurs from concentrated solutions. In fact, in the synthesis of the complexes in aqueous solutions, the complexes were isolated as neutral complexes at their isoelectric points. Cationic complexes can be prepared either by redissolution of the neutral complexes in triflic acid and isolation as triflate salts or by direct synthesis in aprotic solvents with neutral dicarboxylic acid ligand ($4,4'\text{-}dcbpyH_2$).

It has been shown in that in complexes of the type $[Ru(4,4'\text{-}dcbpy)_n(bpy)_{3-n}]$, the carboxybipyridine ligand undergoes successive protonation with pK_a's in the region of 2.8 and 1.7.[25]

$$[Ru(4,4'\text{-}dcbpy)(bpy)(4,4'\text{-}dcbpyH_2)] \rightleftharpoons [Ru(4,4'\text{-}dcbpy)_2(bpy)]^{2-} + 2H^+ \quad pK_a = 2.80 \qquad (1)$$

$$[Ru(bpy)(4,4'\text{-}dcbpyH_2)_2]^{2+} \rightleftharpoons [Ru(4,4'\text{-}dcbpy)(bpy)(4,4'\text{-}dcbpyH_2)] + 2H^+ \quad pK_a = 1.70 \qquad (2)$$

Chelated dpp ligands however are very weakly basic, undergoing protonation only in concentrated acid solutions ($pK_a \leq -3.4$).[25] As indicated in the Experimental Section, in our synthesis of these complexes using neutral $4,4'\text{-}dcbpyH_2$ ligands, the tetracationic binuclear complex was isolated and characterized as the hexafluorophosphate salt.

Absorption spectral changes shown in Figure 2 for the binuclear complexes are similar to that observed during protonation of the mononuclear complexes cited above. The basic form has its absorption maxima at 530, 438, and 298 nm. Protonation of the 4,4'-dcbpy ligands leads to red shifts of the 438- and 298-nm bands to 448 and 306 nm, respectively, and a blue shift of the 530-nm band to 518 nm.

Luminescence. Mixed-ligand complexes such as $[Ru(BL)(LL)_2]$ with bridging ligands (BL) such as dpp or bpym show moderate red-emission in degassed solution at room temperature. Tables III–V present data on the emission maxima lifetimes and quantum yields for different mono- and binuclear complexes in various solvents at room temperature and in MeOH-EtOH glass (4.1, v/v) at 77 K measured in our laboratories. Wherever data are available from the literature for comparison,[8-13,22-24] they are indicated in parentheses. In general, the agreement is better among the emission maxima and lifetimes than among quantum yields. The emission quantum yield measured for mono- and binuclear complexes are an order to magnitude smaller than those reported earlier.

There are two potential candidates for luminescence (BL → Ru CT or LL → Ru CT). The emission in all cases is assigned as due to the BL → Ru CT after the following considerations: (i) emission is considerably red shifted as compared to that of $(bpy)_3$ complexes; (ii) pH dependence of the emission and (iii) redox potential data indicate that the first reduction occurs essentially at the bridging ligand. In mixed-ligand complexes containing multidentate ligands, redox potential measurements serve as a very good guide for the assignment of the excited-state luminescence. In numerous mixed-ligand Ru complexes that have been examined, the emission invariably is from the MLCT state lowest in energy. Redox potential data on the mono- and binuclear complexes containing bpym or dpp as bridging ligand have been reported earlier.[5-7] The first oxidation (Ru(III/II), centered on

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[25] (a) Nazeeruddin, Md. K.; Kalyanasundaram, K. *Inorg. Chem.* **1989**, *28*, 4251. (b) Kirsch de Mesmaker, A.; Jacquet, L.; Nasielski, J. *Inorg. Chem.* **1988**, *27*, 4451 and references cited therein. (c) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170. (d) Lay, P. A.; Sasse, W. H. F. *Inorg. Chem.* **1984**, *23*, 4125.

Table III. Luminescence Properties of MLCT Excited States of Mononuclear Complexes of the Type $[Ru(LL)_2(dpp)]^{2+}$ in Different Solvents at Room Temperature and in EtOH–MeOH Glass (4:1 v/v) at 77 K

LL	solvent	emisison (20 °C)				emission (77 K)	
		λ_{max}, nm					
		cor	uncor	τ, ns	ϕ, %	λ_{max}, nm	τ, μs
Me_2bpy	CH_2Cl_2	685	664	390			
	CH_3CN	702	676	303		640, 690	4.06
	H_2O	729	703	64			
bpy	CH_2Cl_2	667	650	450	1.51		
	CH_3CN	682	660 (660[a])	382 (276[a])	0.92	624, 670	5.36
	EtOH		672 (675[b])	218	(4.9[b])		
	CH_3OH	702	674	210	0.39		
	H_2O	710	688	127 (135[b])			
phen	CH_2Cl_2	632	647	447			
	CH_3CN	647	661 (652[a])	460 (252[a])		565, 612	4.62
	CH_3OH	653	678	290			
	H_2O	656	685	202			
5-Cl-phen	CH_2Cl_2	626		346			
	CH_3CN	677	652	505		570, 615	4.78
	H_2O	680	656	260			
4,4'-$dcbpy^{2-}$	H_2O (pH 7)	684	658	174			
4,4'-$dcbpyH_2$	CH_3OH	688	660	218		607, 650	4.06
dpp	CH_3CN	642	623 (621[a])	203 (183[a])	(4.0[c])	597, 640	5.10
	H_2O	649	629 (636[a])	274 (270[a])			

[a] References 5–7. [b] Reference 11. [c] Reference 12.

Table IV. Luminescence Properties of MLCT Excited States of Mononuclear Complexes of the Type $[Ru(LL)_2(bpym)]^{2+}$ in Different Solvents at Room Temperature and in EtOH–MeOH Glass (4:1 v/v) at 77 K

LL	solvent	emission (20 °C)				emission (77 K)	
		λ_{max}, nm					
		cor	uncor	τ, ns	ϕ, %	λ_{max}, nm	τ, μs
Mixed-Ligand bpym Complexes $[Ru(LL)_2(bpym)]^{2+}$							
bpy	CH_2Cl_2	657		130	0.22		
	CH_3CN	690	662	87	0.17	624, 680	0.87
	CH_3CN	678[a]	(668[a])	91[b]	0.11[d]		
	CH_3OH	703	671	40 (36[b])	0.12		
	H_2O	715	678	15	0.015		
	H_2O		(680[c])	(13[b])			
bpym	CH_3CN	639	131	0.28[d]		616, 674	5.20
	CH_3OH	656	102				
	H_2O	660	83	(9.0[c])			
Binuclear Complexes of Ru(II) of the Type $[(LL)_2Ru]_2(bpym)^{4+}$							
bpy	CH_2Cl_2		770	≤20	≤0.01		
	CH_3CN		790	≤20	≤0.01	702, 770	0.36
	H_2O	824	795	≤15	≤0.01		

[a] References 5–7. [b] Reference 22b. [c] Reference 8. [d] Reference 10a,b.

the metal) occurs at potentials similar to those of the monomeric analogues. The first reduction (Ru(II/I), bridging ligand based) occurs at potentials ca. 400 mV more positive of those of the monomer analogues. Differences in the potential between the first and second oxidation, $\Delta E_{(1/2)}$, are of much interest as they serve as a direct quantitative measure of the communication between the two metal centers through the bridging ligand and on the stability of the mixed valence (Ru^{II}–Ru^{III}) species vs isovalent forms.

Figure 3 presents representative emission spectra of the mono- and binuclear complexes in different solvents. Data presented in Tables III–V show that the emission maxima of dpp and bpym complexes, both of mono- and binuclear types, are very similar. Emission spectra of the binuclear complexes at 77 K are well resolved, showing vibrational progression of ca. 1260 cm^{-1}, typical for transition-metal polypyridyl complexes. The emission decay of the mono- and binuclear complexes followed first-order kinetics. Between the mono- and binuclear complexes, the MLCT excited-state lifetime and emission yields span a wide range. In a given solvent, the emission lifetime of the dpp complex decreases by a factor of 2–3 upon binucleation. The emission lifetimes of the MLCT excited state in the binuclear complexes of dpp are sufficiently long-lived (50–150-ns range) to allow participation in bimolecular photoredox processes in solution.

The effect of binucleation on the luminescence of the bpym complex however is very pronounced. The bpym complexes are comparatively short-lived and are weak emitters. In aqueous solution at room temperature, the emission from the binuclear bpym complex is extremely weak ($\phi = 10^{-6}$) with a maximum around 795 nm. The bpym-bridged binuclear complex has been

Table V. Absorption and Luminescence Properties of MLCT Excited States of Ligand-Bridged Binuclear Polypyridyl Complexes of Ru(II) of the Type $[(LL)_2Ru–dpp–Ru(LL)_2]^{4+}$ in Different Solvents at Room Temperature and in EtOH–MeOH Glass at 77 K

LL	solvent	emission (20 °C)				emission (77 K)	
		λ_{max}, nm					
		cor	uncor	τ, ns	ϕ, %	λ_{max}, nm	τ, μs
bpy	CH_2Cl_2	770	727	154	0.065		
	CH_3CN	790	752	140	0.025	702, 770	2.38
	CH_3CN		(756[a])	(134[a])			
	EtOH		753	84	(0.3[b])		
	EtOH		(755[b])				
	CH_3OH	797	753	100			
	H_2O	800	765	55	0.012		
	H_2O			(54[b])	(0.7[c])		
4,4'-$dcbpy^{2-}$	H_2O (pH 7)	778	738	87			
4,4'-$dcbpyH_2$	H_2O (pH 0)						
	CH_3CN	745	710				
	CH_3OH	763	718	123		699, 765	2.32
phen	CH_3CN		746	153			

[a] Reference 6. [b] Reference 11. [c] Reference 12.

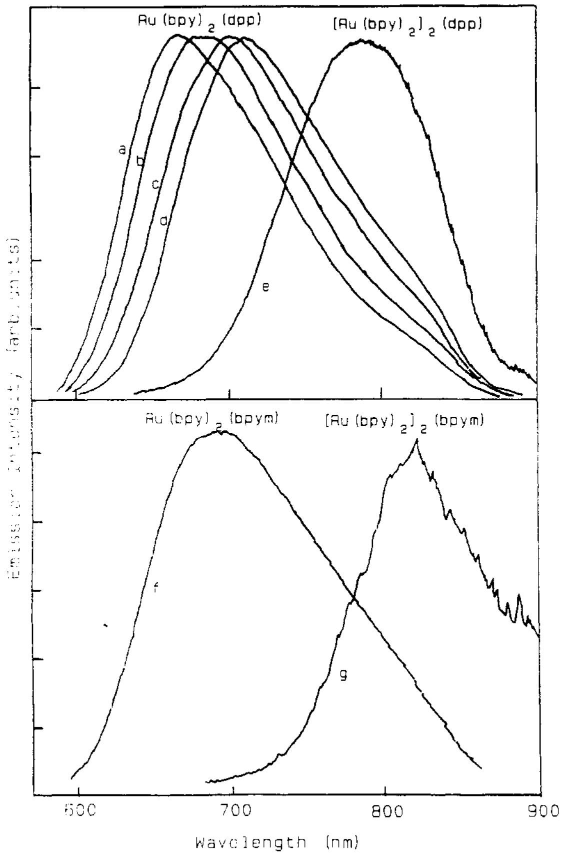

Figure 3. Luminescence spectra of mono- and binuclear complexes of Ru in solution at room temperature (20 °C): (top) $Ru(bpy)_2(dpp)^{2+}$ emission in CH_2Cl_2 (a), CH_3CN (b), CH_3OH (c), and H_2O (d) and $[Ru(bpy)_2]_2(dpp)^{4+}$ dimer emission in CH_3CN (e); (bottom) $Ru(bpy)_2(bpym)^{2+}$ emission in CH_3CN (f) and $[Ru(bpy)_2]_2(bpym)^{4+}$ emission in H_2O (g).

reported[8,10,13] to be nonluminescent in solution at room temperature. It is unfortunate that, in one of the widely quoted studies on the emission properties of the binuclear bpym complex,[9] the photomultiplier used lacked photoresponse in the red region(!) to unambiguously detect the emission. The binuclear bpym complex is rather unstable in organic solvents, and in our opinion, it is the instability of these complexes that complicates measurements.

It can be noted from Tables III–V that, with solvents of increasing polarity, the emission spectra show increasing red shifts in maxima and decreased lifetime and yields. From the measured lifetimes (τ) and quantum yields (ϕ_r), the radiative (k_r) and nonradiative rate constants (k_{nr}) can be evaluated according to eqs 3 and 4. The calculated rate constant k_r is about (2.4–3.0)

$$k_r = \phi\tau^{-1} \tag{3}$$

$$k_{nr} = (1 - \phi)\tau^{-1} \tag{4}$$

× 10^4 s^{-1}, independent of the media. The solvent order in influencing the spectral shifts, lifetimes, and yields is as follows: $CH_2Cl_2 < CH_3CN < CH_3OH < H_2O$. Clearly the lifetimes and quantum yields of luminescence are controlled by nonradiative relaxation, which increases in protic solvents. Meyer et al.[24f] have shown that it is possible to correlate the effect of solvent on the nonradiative decay constant in several polypyridyl complexes of Ru, Os, and Re on the basis of the energy gap law for radiationless transitions.

There have been a few attempts to correlate the solvent sensitivity of the luminescence from the LL → M CT excited state in polypyridyl complexes: $M(LL)_3$,[25] $M(LL)_2(CN)_2$,[26] and $[M(CO)_4(LL)]$.[27] The solvent effect observed in the present mixed-ligand complexes are much more pronounced (>40 nm) than what has been observed earlier for $Ru(bpy)_3^{2+}$. The spectral shifts follow Gutman's acceptor number (AN) of the solvent.[27d] It is very likely that the spectral shifts derive largely from the solvent sensitivity of Ru(II)–Ru(III) potentials as the potentials of $(LL)/(LL)^-$ couples are much less solvent dependent.

As regards the *cationic and anionic binuclear complexes involving 4,4′-dcbpy*, it was mentioned earlier that the absorption spectra of the two forms are different. In aqueous solutions, upon decreasing of pH, the emission also blue shifts with increasing intensity. Figure 2 (bottom) presents some representative emission spectra at four selected pH values. The spectral shifts occur in the same pH range as the absorption, following a similar pH profile. The more intense emission from the protonated form of the binuclear complex is analogous to the behavior observed with $Ru(4,4'\text{-dcbpy})_2(bpy)$ but is in distinct contrast to that observed with $Ru(4,4'\text{-dcbpy})_2(dpp)$. The direct correspondence between the pH range over which blue shifts in the emission occur with that of the absorption suggest a change in the nature of the complex that is being excited at different pH values. In the absence of detailed knowledge on each of the partially protonated forms of the complex, we have included in Tables I and III absorption and emission data at two pH values of 7.0 and 0 (1 N HCl).

Spectator Ligand Effects. Absorption and luminescence data presented in various tables clearly show that these properties are very sensitive to the fine tuning of the spectator ligand LL. In the series Me_2bpy, bpy, phen and 5-Cl-phen, both the M–BL absorption and emission blue shift with considerable lengthening of the excited-state lifetime. For a small shift of the Ru(2+/+) potential (less than 200 mV), the variation in the luminescence maxima, lifetime, and yields is very pronounced indeed. The above energy ordering follows the electron-releasing or -withdrawing power of the spectator ligand. For example, it is reasonable to expect the Me_2bpy ligand to increase the electron density, destabilizing the d–π level. The point is that the spectator ligand effects in influencing photophysical properties are nonnegligible.

Similar to the behavior observed in $Ru(4,4'\text{-dcbpy})_n(bpy)_{3-n}$ (n = 1, 2 and 3), the dpp complexes with 4,4′-dcbpy have more intense emission and longer lived excited states. Incidentally, among the various binuclear polypyridyl Ru complexes known to date, the complex $Ru(4,4'\text{-dcbpy})_2]_2(dpp)$ reported here, has the longest lived MLCT excited state in solution at room temperature.

Excited-State Absorption Spectra. Excited-state absorption spectra provide a direct means of monitoring the nature of charge distribution in the excited state and also for quantitative analysis of excited-state redox processes. Figures 4 and 5 present transient absorption (difference) spectra, corresponding to the MLCT excited state of the mono- and binuclear complexes with dpp and bpym as bridging ligands. The assignment of the transient absorption as due to the excited state of the binuclear complex is based on the similarity of the transient decay with the emission. The binuclear complexes are stable to photolysis in water and in organic solvents such as methylene chloride or acetonitrile, as indicated by the quantitative recovery of the ground-state binuclear complex after several laser pulse excitations.

The MLCT excited-state absorption spectra shown in Figures 4 and 5 are typical of polypyridyl Ru complexes with several absorption minima corresponding to the absorption of ligand π–π^*, M–L charge transfer and $(LL)^-$ or $(BL)^-$ absorption bands. The mononuclear *bpym* complex spectrum shown in CH_2Cl_2 is very similar but with better spectral resolution than that reported earlier[24] for the same complex in water. Table VI provides a summary of various absorption maxima of the transients along with their assignments. Data on the mixed-ligand complexes are

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(26) (a) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, *101*, 6571. (b) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. In *Photophysics and Photochemistry of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer Verlag: Berlin, 1987; p 159.

(27) (a) Manuta, D.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825. (b) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *26*, 3306. (c) Burgess, J.; Chambers, J. G.; Haines, R. I. *Transition Met. Chem.* (*Weinheim, Ger.*) **1981**, *6*, 145. (d) Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661.

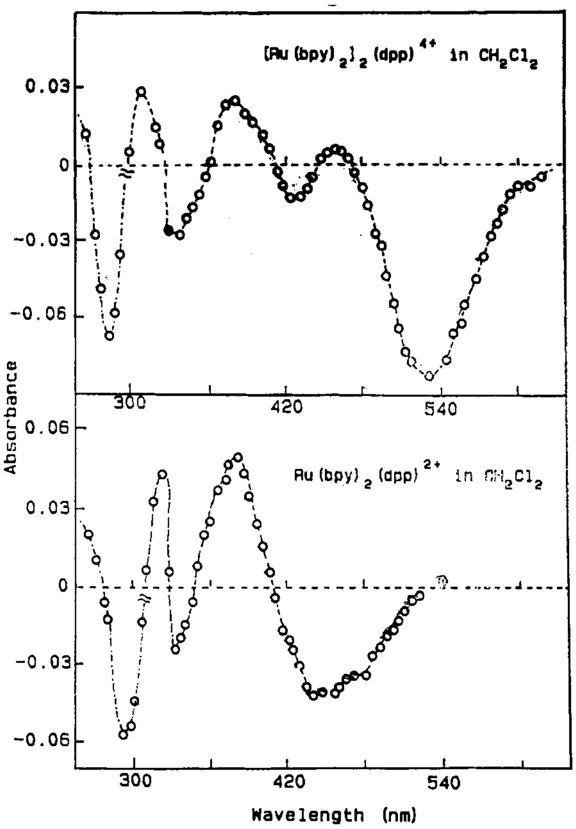

Figure 4. Transient absorption spectra corresponding to the MLCT excited state of $Ru(bpy)_2(dpp)^{2+}$ (bottom) and $[Ru(bpy)_2]_2(dpp)^{4+}$ (top) in CH_2Cl_2. Spectra were recorded at ca. 50 ns after laser pulse excitation.

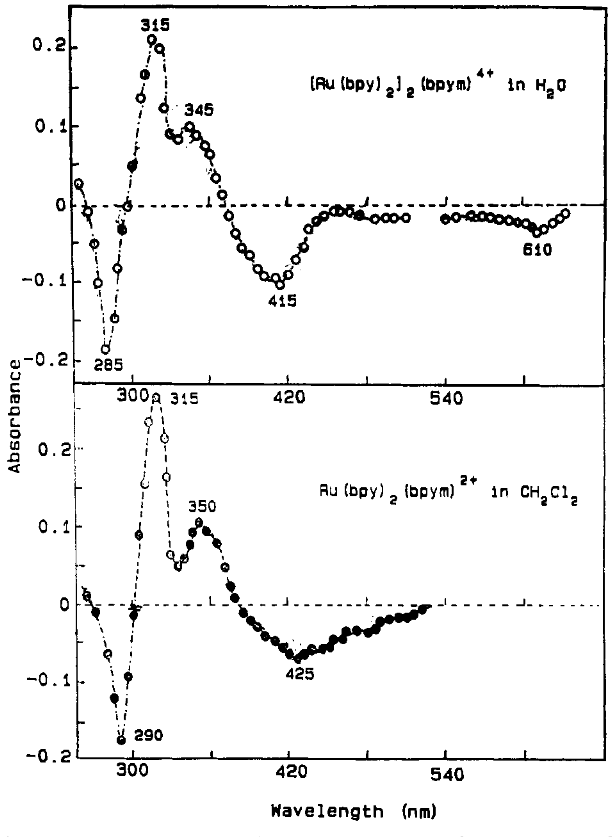

Figure 5. Transient absorption spectra corresponding to the MLCT excited state of $Ru(bpy)_2(bpym)^{2+}$ in CH_2Cl_2 (bottom) and $[Ru(bpy)_2]_2(bpym)^{4+}$ (top) in H_2O. Spectra were recorded at ca. 10 ns after laser pulse excitation.

very instructive. The presence of a localized electron on the bridging ligand in the excited state is clearly seen by the presence of absorption bands, characteristic of $(BL)^-$ rather than those of $(LL)^-$.[28]

Table VI. Various Absorption Maxima Observed in the Excited-State Absorption Spectra of Ru-Polypyridyl Complexes and Their Assignments

abs max, nm	assignt	complexes where obsd
310	π-π* (4,4'-dcbpy)	$Ru(4,4'\text{-dcbpy})_3^{2+}$
315	π-π* (bpy)	$Ru(bpy)_3^{2+}$, $[(bpy)_2Ru]_n(BL)$ (n = 1, 2)
330	π-π* (bpym)	$Ru(bpym)_3^{2+}$
335	π-π* (bpz)	$Ru(bpz)_3^{2+}$
345	π-π* (dpp)	$Ru(dpp)_3^{2+}$
345	bpym$^-$	$Ru(bpym)_3^{2+}$, $[(bpy)_2Ru]_n(bpym)$ (n = 1, 2)
370	dpp$^-$	$Ru(dpp)_3^{2+}$, $[(bpy)_2Ru]_n(dpp)$ (n = 1, 2)
375	bpy$^-$, 4,4'-dcbpy$^-$, bpz$^-$	$Ru(bpy)_3^{2+}$, $Ru(4,4'\text{-dcbpy})_3^{2+}$, $Ru(bpz)_3^{2+}$
445	Ru-bpy CT	$Ru(bpy)_3^{2+}$
460	Ru-bpym CT	$[(bpy)_2Ru]_n(BL)$, (n = 1, 2)
460	Ru-dpp CT	$[(bpy)_2Ru]_n(BL)$, (n = 1, 2)

For the binuclear bpym complex, the emission intensity in solution was too weak to be able to measure the emission lifetime. In laser flash photolysis experiments, the bleaching recovery of the ground-state absorption occurs very rapidly along with the excitation pulse (ca. 8 ns), suggesting the excited state lifetime to be ≤15 ns. We are in the process of making time-resolved absorption studies with a shorter (80-ps) laser pulse to obtain a more accurate lifetime.

Note Added during the Revision. Since the completion of this work, Petersen et al.[31] have reported on the redox and photophysical properties of binuclear complexes of dpp, $\{[(LL)_2Ru]_2(dpp)\}^{4+}$, where LL = bpy and phen. Our results are in excellent agreement with this work.

II. Photoredox Reactions and Dynamics of Oxidative Cleavage of the Binuclear Complexes. An attractive possibility in the polynuclear complexes is to carry out single-electron- as well as multielectron-transfer processes. The ease of oxidation or reduction and the reversibility and stability of the various oxidized or reduced forms are of paramount importance in determining the efficiency of these complexes to serve as multielectron-transfer photocatalysts or relays. We have examined several homo (Ru-Ru) binuclear complexes with different bridging ligands for the above criteria in both thermal and photoredox processes. A topic of much concern and interest in the redox chemistry of polynuclear complexes is focused on the mixed-valence species. We have carried out some preliminary studies of photooxidation of the binuclear complexes in the (II,II) state in aqueous solution, and the results are outlined below.

Photochemical Oxidation of the (II,II) Complex with Persulfate. Given the fact that the MLCT excited state of the (II,II) binuclear complex is fairly long-lived in degassed solutions at room temperature, it is tempting to examine photochemical oxidation with one- and two-electron acceptors. Estimates of the redox properties of the MLCT excited state of the binuclear complexes are available. In general, in the excited state the binuclear complexes are weaker reductants. [$E^{2+*/3+}$ = -0.53, -0.34 V (vs NHE) for the dpp monomer and bimetallic complex respectively.[11,12]] We found that the one-electron acceptor methyl viologen (E_0 = -0.44 V) does not quench the luminescence of the binuclear dpp complex, in good agreement with these estimates.

Persulfate was chosen as the electron acceptor due to (i) the absence of any dark (thermal) oxidation of the (II,II) complex, (ii) its possible role as a sequential two-electron acceptor, and (iii) the lack of absorption in the visible region to facilitate clear spectral analysis. Visible-light irradiation of the various (II,II) complexes

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[28] (a) Heath, G. A.; Yellowlees, L. J.; Braterman, P. *J. Chem. Soc., Chem. Commun.* **1981**, 287. (b) Elliott, M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 751. (c) Donohue, R. J.; Tait, C. D.; DeArmond, M. K.; Wertz, D. W. *Spectrochim. Acta* **1986**, *42A*, 233.

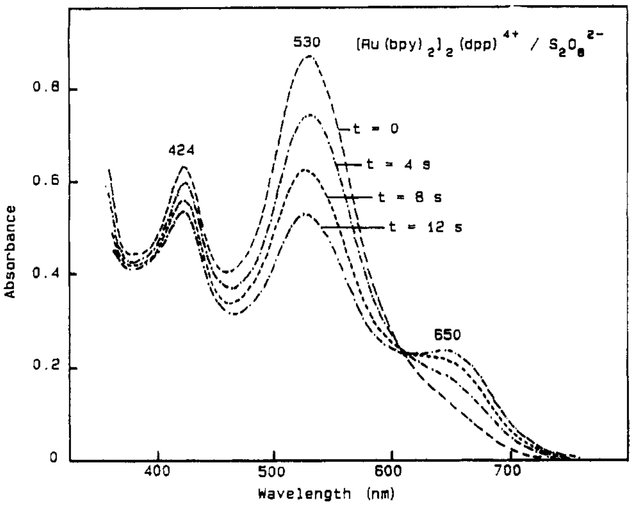

Figure 6. Absorption spectral changes observed during the visible-light photolysis ($\lambda \geq 495$ nm) of $[Ru(bpy)_2]_2(dpp)^{4+}$ (4×10^{-5} M) in aqueous solutions containing $K_2S_2O_8$ (4×10^{-3} M, pH 9.0).

in the persulfate was found to cause significant, permanent spectral changes. Depending on the conditions and extent of photolysis, the photoproduct(s) could be reduced back to the starting (II,II) state by using a strong reductant such as dithionite. Figure 6 presents typical spectral changes occurring during the visible-light photolysis ($\lambda \geq 495$ nm) of the (II,II) state of the homobinuclear Ru-dpp complex $[Ru(bpy)_2]_2(dpp)^{4+}$ (ca. 40 μM) in aqueous solutions (pH 9.0) containing $S_2O_8^{2-}$ (5×10^{-4} M). Oxidation of the Ru-dpp homobinuclear complex leads to formation of a product with an absorption maximum at 650 nm ($\epsilon = 10000$ M^{-1} cm^{-1}). During the course of oxidation, the absorption maxima at 530 and 424 nm slowly blue shift, with an isobestic point located at 612 nm.

Figure 7 presents absorption spectral changes observed during visible-light irradiation of the binuclear complex with bis(4,4'-dicarboxy-2,2'-bipyridine) as spectator ligands $[Ru(4,4'\text{-}dcbpy)_2]_2(dpp)^{4-}$ under similar photolysis conditions. At early stages of photolysis, clean isobestic points are maintained and the photoproduct can be reduced back to the (II,II) state as indicated by the spectrum of the reduction product (labeled as P_i in Figure 7). On the basis of the quantitative reduction of this product to the (II,II) complex with sodium dithionite, we assign it to the (II,III) state in the binuclear complex (reaction 5). Extensive photolysis leads to formation of dithionite reduction products, different from the reactants, that are possibly cleaved mononuclear fragments (labeled as P_f in Figure 7).

The photooxidation presumably occurs in two steps, as documented in several other cases:[29]

$$[L_2Ru^{II}\text{-}dpp\text{-}Ru^{II}L_2]^{4+*} + S_2O_8^{2-} \rightarrow [L_2Ru^{II}\text{-}dpp\text{-}Ru^{III}L_2]^{5+} + S_2O_8^{3-} \quad (5)$$

$$S_2O_8^{3-} \rightarrow SO_4^{2-} + SO_4^{-} \quad (6)$$

The intermediate species SO_4^- being a strong oxidant can oxidize either a second molecule of the (II,II) complex (reaction 7) or oxidize the (II,III) complex to its (III,III) form (overall reaction indicated by reaction 8). We find that partial oxidation of the

$$[L_2Ru^{II}\text{-}dpp\text{-}Ru^{II}L_2]^{4+} + SO_4^{-} \rightarrow [L_2Ru^{II}\text{-}dpp\text{-}Ru^{III}L_2]^{5+} + SO_4^{2-} \quad (7)$$

$$[L_2Ru^{II}\text{-}dpp\text{-}Ru^{II}L_2]^{4+*} + S_2O_8^{2-} \rightarrow [L_2Ru^{III}\text{-}dpp\text{-}Ru^{III}L_2]^{6+} + 2SO_4^{2-} \quad (8)$$

$$[L_2Ru^{III}\text{-}dpp\text{-}Ru^{III}L_2]^{6+} \rightarrow [L_2Ru^{III}(dpp)]^{3+} + [L_2Ru^{III}(X)_2]^{3+} \quad (9)$$

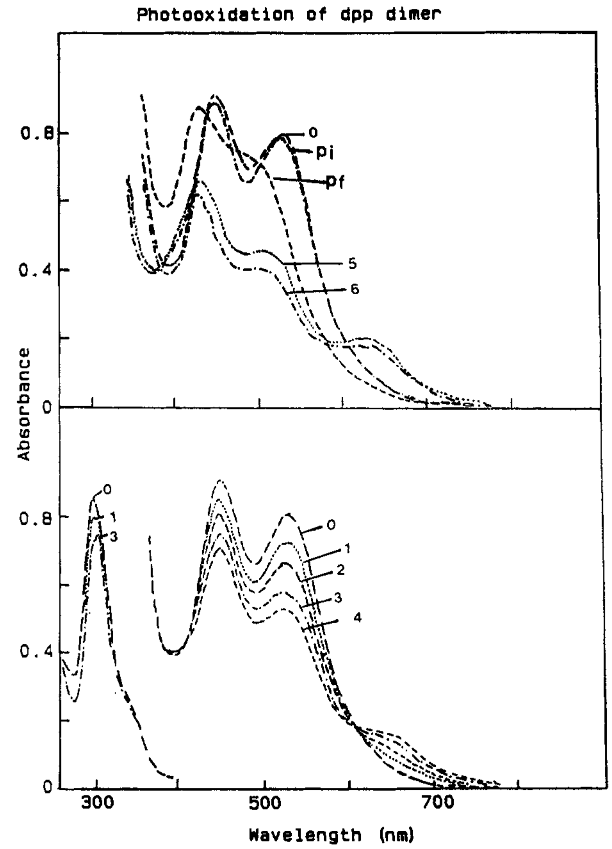

Figure 7. Absorption spectral changes observed during the visible-light photolysis ($\lambda \geq 495$ nm) of $[Ru(4,4'\text{-}dcbpy)_2]_2(dpp)^{4-}$ (2×10^{-5} M) in aqueous solutions containing $K_2S_2O_8$ (4×10^{-3} M, pH 9.0). Spectra labeled 0-6 correspond to spectra recorded after 0-6 min of photolysis ($\lambda \geq 495$ nm). P_i and P_f refer to spectra of products obtained upon dithionite reduction of photolysis solutions after 4 and 6 min of photolysis, respectively.

(II,II) complex to the (II,III) complex followed by reduction with sodium dithionite leads to nearly quantitative recovery of the (II,II) state provided that (i) a low concentration of the quencher (persulfate) is used and (ii) that photolysis is restricted to low conversions, ≤30% (concentration of the (II,III) dimer to ca. 20 μM).

It may be noted that spectral changes for the cationic bpy complex are extensive after brief photolysis of about 20 s. Photolysis of the anionic 4,4'-dcbpy complex under similar conditions is inefficient. Comparable spectral changes are observed only after several minutes of irradiation with a 10-fold excess of persulfate. The differences in the photooxidation efficiencies of the binuclear complexes with bpy or 4,4'-dcbpy as spectator ligands are readily understood as due to electrostatic effects on the probability of the excited-state-complex-quencher encounters. The bpy complex is overall tetracationic $[(bpy)_2Ru]_2(dpp)^{4+}$, while the analogous 4,4'-dcbpy complex is overall tetraanionic $[(4,4'\text{-}dcbpy)_2Ru]_2(dpp)^{4-}$. So it is likely that in the former complex ion pairing promotes the probability of the encounter in the excited state. Small blue shifts observed in the ground-state absorption spectrum of the binuclear complex upon persulfate addition indicate such ion pairing.

For the 4,4'-dcbpy complex $[(4,4'\text{-}dcbpy)_2Ru]_2(dpp)^{4-}$, an excited-state quenching rate constant of 2.6×10^8 M^{-1} s^{-1} in nonbuffered solutions has been determined (reaction 5) via normal Stern-Volmer plots of the emission intensity. As a bimolecular reaction between a tetraanion and a dianion, the quenching process is subject to significant ionic-strength effects. Attempts to determine the efficiency of excited-state quenching and the extent of ion pairing in the cationic bpy complex $[(bpy)_2Ru]_2(dpp)^{4+}$ yielded nonreproducible results, due to the extreme photosensitivity of the Ru complex-quencher solutions. To confirm the spectral assignments of the photoproducts outlined above, thermal and

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[29] (a) Neumann-Spallart, M.; Kalyanasundaram, K.; Grätzel, C.; Grätzel, M. *Helv. Chim. Acta* **1980**, *63*, 1111. (b) Bolletta, F.; Juris, A.; Maestri, M.; Balzani, V. *Inorg. Chim. Acta* **1980**, *44*, L175. (c) White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891.

electrochemical oxidation of the dimers were also examined.

In analogous photolysis studies with the bpym complex, $[(bpy)_2Ru]_2(bpym)^{4+}$, concurrent with the decrease in the absorption bands of the starting complex, there is only a rising shoulder in the red (starting at 800 nm) with an isobestic point located at 640 nm (spectra not shown). Control of reversibility by dithionite reduction along the lines indicated earlier showed that oxidation is irreversible even in the early stages of photolysis. Presumably rapid dismutation of the (II,III) complex is responsible for the observed results. Meyer et al., in their studies,[13] have reported that the mixed-valence (II,III) bpym complex $[(bpy)_2Ru–bpym–Ru(bpy)_2]^{5+}$ prepared via controlled-potential electrolysis is unstable.

Thermal and Electrochemical Oxidation of the (II,II) Complex. In their studies on the Ru binuclear complexes with dpp as the bridging ligand, Gafney et al.[11] have reported that chemical oxidation of the binuclear complexes in the (II,II) state with ceric ammonium sulfate in aqueous D_2SO_4 resulted in the cleavage of the dimer and that addition of $NaNO_2$ after Ce^{4+} oxidation recovered <10% of the original dimeric complex (eqs 10 and 11).

$$[L_2Ru^{II}\text{–dpp–}Ru^{II}L_2]^{4+} \rightarrow [L_2Ru^{II}\text{–dpp–}Ru^{III}L_2]^{5+} \quad (10)$$

$$[L_2Ru^{II}\text{–dpp–}Ru^{III}L_2]^{5+} \rightarrow [L_2Ru^{II}(dpp)]^{2+} + [L_2Ru^{III}(X)_2]^{3+} \quad (11)$$

Since the cyclic voltammetric studies in acetonitrile showed reversible waves for the first and second oxidation waves we wondered whether the (II,III) and (III,III) intermediates were substitutionally labile, leading to cleavage products. We examined carefully the chemical oxidation of the (II,II) complexes (ca. 50 μM) with Ce^{4+}. Extensive oxidation (beyond 30%) with a large excess of the oxidant leads to substantial cleavage of the (II,II) binuclear complex to the monomeric fragments, as evidenced by the absorption spectra of the dithionite reduction product.

We also examined the electrochemical oxidation and reversibility of the oxidation waves. We confirm the redox potentials for the first two oxidations and their reversibility at fast scan rates (≥200 mV/s). The second oxidation wave is only partially reversible at slower scan rates. Controlled-potential electrolysis of the (II,II) complex in acetonitrile at 1.40 V (vs SCE), which corresponds to the first oxidation wave, leads to spectral changes identical with those observed above under controlled chemical oxidation. The product, with the absorption maximum at 645 nm, (II,III) state, can be quantitatively reduced to the (II,II) state upon potential reversal without loss. At low concentrations (≤20 μM), we have not observed any significant decay of the (II,III) complex over a period of several hours.

It is likely that, in chemical oxidations with an excess of the oxidant or electrochemical oxidations at ≥30% conversion, preferential oxidation of the (II,III) complex to the (III,III) state occurs (in place of oxidation of residual (II,II) complexes) and subsequent rapid cleavage of the (III,III) species (reactions 10 and 11). The above results are consistent with those of photochemical oxidation with persulfate discussed above.

The rapid cleavage of the binuclear complexes in the (III,III) state to its monomeric components probably arises due to the loss of π-back-bonding forces present in the (II,II) complex and to the fact that pyrazine N centers are poor ligands by themselves.[30] The stability of the mixed-valence species such as (II,III) vs comproportionation to give (II,II) and (III,III) dimers have been of much interest:

$$2(\text{II,III}) \rightarrow (\text{II,II}) + (\text{III,III}) \quad (12)$$

Theoretical estimates for the comproportionation constant, based on peak separation in the electrochemical oxidation of the dimers, have been obtained earlier for several ligand-bridged binuclear complexes of the type under scrutiny. The ability to generate chemically or photochemically the (II,III) complexes should allow a direct experimental measure of the comproportionation phenomenon and its consequences. Petersen et al. have calculated[7] comproportionation constants of 5×10^2 and 1.1×10^3 for $[Ru(bpy)_2]_2(dpp)$ and $[Ru(bpy)_2]_2(bpym)$, respectively. Unfortunately, as explained above, we could generate only low concentrations of the (II,III) complexes. The concentration is too low to permit monitoring of the weak intervalence bands in the near-IR region or monitoring of the concentration dependence of the decay of the mixed-valence species.

Concluding Remarks

By a comprehensive study of the photophysical properties of a series of complexes in several solvents, it has been possible to clarify the origin of wide differences and inconsistencies in the reported behavior of two representative cases of ligand-bridged mono- and binuclear complexes of Ru. The present studies also largely extended their photophysics and photoredox chemistry by providing new information on the excited-state tunability, absorption, solvent sensitivity, and redox reactivity. Initial results on the chemical and photochemical oxidation are encouraging, and more detailed studies on the binuclear complexes with mixed-valence and higher oxidation states are in progress. While the dpp complexes appear as good candidates for detailed scrutiny, instability problems restrict considerably the utility of bpym-based binuclear complexes. (For related studies on binuclear complexes of Os(II) and Re(I), see refs 32 and 33.)

Acknowledgment. It is a pleasure to acknowledge enlightening discussions on various aspects of this work with Prof. Michael Grätzel and Dr. F. Rotzinger. This work has benefitted with financial support from the Swiss Federal Office for Energy Research (NEFF) and the Government of India (Md.K.N).

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