

Utilization of substituted polyazine bridging ligands to tune the spectroscopic and electrochemical properties of bimetallic ruthenium complexes

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Abstract

The polyazine bridging ligands Cl₂dpq and Me₂dpq (where Cl₂dpq = 6,7-dichloro-2,3-bis(2'-pyridyl)quinoxaline and Me₂dpq = 6,7-dimethyl-2,3-bis(2'-pyridyl)quinoxaline) have been synthesized and their electrochemical and spectroscopic properties studied. Cl₂dpq is easier to reduce than the unsubstituted dpq (dpq = 2,3-bis(2'-pyridyl)quinoxaline) ligand by 250 mV, while Me₂dpq is harder to reduce than dpq by 180 mV. These two substituted dpq ligands, along with dpp, dpq and dpb (dpp = 2,3-bis(2'-pyridyl)pyrazine and dpb = 2,3-bis(2'-pyridyl)benzoquinoxaline), give a series of five polyazine bridging ligands which provide a similar coordination environment to metals. In addition, this series of ligands makes possible the systematic variation of the energy of the lowest unoccupied molecular orbital (LUMO), the bridging ligand based π^* . The relative energy of the π^* orbitals is dpp > Me₂dpq > dpq > Cl₂dpq > dpb. The new monometallic and bimetallic systems of the form [(bpy)₂Ru(BL)]²⁺ and [(bpy)₂Ru]₂(BL)⁴⁺ (where BL = Me₂dpq and Cl₂dpq) have been synthesized and their spectroscopic and electrochemical properties studied. In addition, the previously studied systems with dpp, dpq and dpb as the bridging ligand have been prepared and their properties are reported herein for comparison. The metal complexes become easier to reduce as a function of bridging ligand with $E_{1/2}(\text{reduction})$ for dpp < Me₂dpq < dpq < Cl₂dpq < dpb. The energy of the lowest metal-to-ligand charge transfer (MLCT) band, Ru(d π) → BL(π^*), as well as the emission energy, shift to lower energy as a function of bridging ligand with E_{abs} or E_{em} for dpp > Me₂dpq > dpq > Cl₂dpq > dpb. These results indicate that it is possible to tune the spectroscopic and electrochemical properties of multimetallic complexes through the incorporation of substituent groups on polyazine bridging ligands.

Introduction

Considerable attention has focused on the spectroscopic and electrochemical properties of Ru(bpy)₃²⁺ due to the ability of this complex to absorb visible light and undergo excited state electron- and energy-transfer (bpy = 2,2'-bipyridine) [1]. In an effort to tune the excited- and ground-state properties of ruthenium polypyridyl complexes, a series of closely related systems has been studied which incorporate substituted bipyridines and phenanthrolines [2]. The utilization of such complexes in photochemical energy conversion and storage systems has been limited, due in part to the inefficiencies inherent in the collisional processes required for excited state energy or electron transfer utilizing such single metal systems. Therefore, recent attention has been focused on the development of multimetallic systems which incorporate the Ru^{II}(bpy)₂

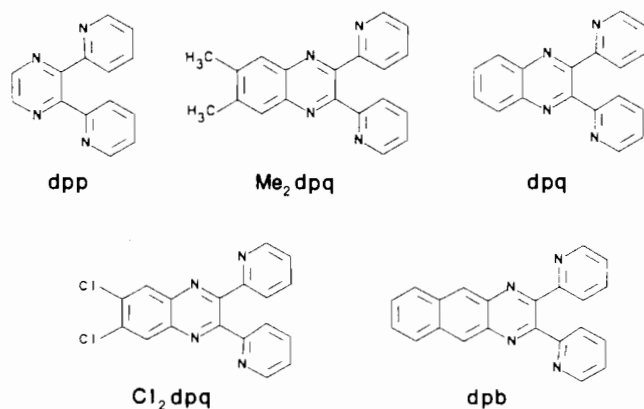
moiety [3]. A great deal of this effort has focused on the utilization of polypyridyl bridging ligands [3].

The lowest lying excited state in these polypyridyl bridged systems is often a bridging ligand based MLCT (Ru(d π) → BL(π^*)). Since the nature and energy of the lowest lying excited state often dominates photo-reactivity, the ability to systematically vary the energy of this state would be extremely useful. Therefore, it would be advantageous to have a series of bridging ligands with π^* orbitals of varying energy, containing similar environments for coordination to two metal centers. This variation in the energy of the ligand based π^* orbital will make possible the tuning of the spectroscopic and electrochemical properties of multimetallic systems.

In an effort to study the effects of the systematic variation of the bridging ligand, we have synthesized two substituted bridging ligands, Me₂dpq and Cl₂dpq. Although these ligands have been previously prepared, they were studied in a non-bridging mode of coordi-

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nation as spectrophotometric reagents for iron(II) and copper(I) [4]. In this application, it is thought that the ligands coordinate through the two pyridine rings without coordination to the substituted quinoxaline portion of the system. The structures of the two substituted dpq ligands, along with dpp, dpq and dpb [3, 4] are shown below.



These ligands have been used to synthesize the mono- and bimetallic ruthenium bipyridine systems: $[(bpy)_2Ru(Me_2dpq)]^{2+}$, $[(bpy)_2Ru(Cl_2dpq)]^{2+}$, $\{[(bpy)_2Ru]_2(Me_2dpq)\}^{4+}$ and $\{[(bpy)_2Ru]_2(Cl_2dpq)\}^{4+}$. The electrochemical and spectroscopic properties of these systems have been studied. Along with the previously prepared dpp, dpq and dpb mono- and bimetallic systems [5] it is possible to systematically tune the ground- and excited-state properties within a multi-metallic framework.

Experimental

Materials

Materials used were reagent grade and used without further purification. The ruthenium trichloride was obtained through the precious metal loan program from Johnson Matthey. 2,2'-Bipyridine was purchased from Fisher Scientific. The acetonitrile (Burdick and Jackson) used in the electrochemical and spectroscopic studies was spectroquality and was dried over activated molecular sieves. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH), was synthesized by the reaction of tetrabutylammonium bromide with hexafluorophosphoric acid, in ethanol. The resulting solid was separated by vacuum filtration and recrystallized several times from hot ethanol and stored in a vacuum desiccator. The adsorption alumina used for purification of the metal complexes was obtained from Fisher Scientific. 2,2'-Pyridyl, phenylenediamine, dichlorophenylenediamine and dimethylphenylenediamine were purchased from Aldrich Chemical Company

and used as supplied. All other chemicals used were Fisher Scientific reagent grade and used without further purification.

Syntheses

2,3-Bis(2'-pyridyl)quinoxaline (dpq)

This was prepared according to the method of Goodwin and Lions by the reaction of *o*-phenylenediamine and 2,2'-pyridyl in ethanol [4a]. $[Ru(bpy)_2Cl_2]$ was prepared by the method of Sullivan *et al.* [6]. $[(bpy)_2Ru(dpp)](PF_6)_2$, $[(bpy)_2Ru(dpq)](PF_6)_2$, $[(bpy)_2Ru(dpb)](PF_6)_2$, $\{[(bpy)_2Ru]_2(dpp)\}(PF_6)_4$, $\{[(bpy)_2Ru]_2(dpq)\}(PF_6)_4$ and $\{[(bpy)_2Ru]_2(dpb)\}(PF_6)_4$ were prepared according to the published procedures [3, 5].

6,7-Dichloro-2,3-bis(2'-pyridyl)quinoxaline

The ligand Cl_2dpq was synthesized by a modification of the synthesis of dpq, substituting 4,5-dichloro-1,2-phenylenediamine for phenylenediamine [4]. The crude product obtained from this reaction must be recrystallized several times from hot ethanol to yield a colorless crystalline product. Purity of the Cl_2dpq was established by thin layer chromatography and NMR spectroscopy. A typical yield for this reaction is 75%.

6,7-Dimethyl-2,3-bis(2'-pyridyl)quinoxaline

The ligand Me_2dpq was synthesized by a modification of the synthesis of dpq, substituting 4,5-dimethyl-1,2-phenylenediamine for phenylenediamine [4]. The crude product obtained from this reaction must be recrystallized several times from hot ethanol to yield a colorless crystalline product. Purity of the Me_2dpq was established by thin layer chromatography and NMR spectroscopy. A typical yield for this reaction is 80%.

Bis(2,2'-bipyridyl)6,7-dichloro-2,3-bis(2'-pyridyl)quinoxalineruthenium(II) dihexafluorophosphate and tetrakis(2,2'-bipyridyl)(μ-6,7-dichloro-2,3-bis(2'-pyridyl)quinoxaline)diruthenium(II) hexafluorophosphate

$[(bpy)_2Ru(Cl_2dpq)](PF_6)_2$ and $\{[(bpy)_2Ru]_2(Cl_2dpq)\}(PF_6)_4$ can be prepared by the reaction of $[Ru(bpy)_2Cl_2]$ (0.420 g, 0.868 mmol) and the ligand Cl_2dpq (0.206 g, 0.584 mmol) in refluxing ethanol/water. The two solids were added to 10 ml of ethanol and 5 ml of water. The suspension was then heated at reflux for *c.* 2 h which resulted in the formation of a purple solution. The reaction mixture was added to 100 ml of saturated aqueous KPF_6 . The solid that formed upon addition of the reaction mixture to saturated $KPF_6(aq)$ was separated by vacuum filtration and washed with 20 ml of ethanol and three 30 ml portions of diethyl ether. The crude product was purified by column chromatography using adsorption alumina developed with

a 2:3 toluene/acetonitrile mixture. The first band that eluted was orange in color and was the monometallic complex, $[(bpy)_2Ru(Cl_2dpq)](PF_6)_2$. This solution was concentrated by rotary evaporation, and added to diethyl ether to induce precipitation of the monometallic complex. The second band eluted was the bimetallic system, $\{[(bpy)_2Ru]_2(Cl_2dpq)\}(PF_6)_4$, and was purple in color. This solution was similarly concentrated by rotary evaporation, and added to diethyl ether to induce precipitation of the bimetallic system. Both the mono- and bimetallic complex were further purified separately by an additional chromatographic step on alumina as described above. Purity of the mono- and bimetallic systems was established by thin layer chromatography. *Anal. Calc.* for $[(bpy)_2Ru(Cl_2dpq)](PF_6)_2$: C, 43.19; H, 2.48; N, 10.61. Found: C, 43.33; H, 2.46; N, 10.42%. *Calc.* for $\{[(bpy)_2Ru]_2(Cl_2dpq)\}(PF_6)_4$: C, 39.58; H, 2.40; N, 9.55. Found: C, 39.12; H, 2.30; N, 9.46%.

Bis(2,2'-bipyridyl)6,7-dimethyl-2,3-bis(2'-pyridyl)quinoxalineruthenium(II) dihexafluorophosphate and tetrakis(2,2'-bipyridyl)(μ-6,7-dimethyl-2,3-bis(2'-pyridyl)quinoxaline)diruthenium(II) hexafluorophosphate

$[(bpy)_2Ru(Me_2dpq)](PF_6)_2$ and $\{[(bpy)_2Ru]_2(Me_2dpq)\}(PF_6)_4$ can be prepared by an analogous procedure as described above for the Cl_2dpq analogues substituting Me_2dpq (0.182 g, 0.582 mmol) for the Cl_2dpq used above. Purity of the mono- and bimetallic systems was established by TLC. *Anal. Calc.* for $[(bpy)_2Ru(Me_2dpq)](PF_6)_2$: C, 47.30; H, 3.17; N, 11.03. Found: C, 47.06; H, 3.32; N, 11.06%. *Calc.* for $\{[(bpy)_2Ru]_2(Me_2dpq)\}(PF_6)_4$: C, 41.92; H, 2.81; N, 9.78. Found: C, 41.62; H, 2.85; N, 9.56%.

Spectroscopy

Absorption spectra were recorded on a Hewlett Packard 8452 diode array spectrophotometer (resolution 2 nm) interfaced to a Hewlett Packard Vectra ES computer. Solutions were prepared using spectroquality acetonitrile

Emission spectra were recorded on a Photon Technology Inc. MSIII spectrofluorometer utilizing a 150 W xenon arc lamp excitation source and a single photon counting detection system with a Hamamatsu R666S red-sensitive photomultiplier tube. This system was interface to a computer for data manipulation and handling. All spectra are uncorrected.

Lifetime measurements

Emission lifetime measurements were made utilizing a Photon Technology Inc. PL 2300 nitrogen laser equipped with a PL 201 high-power continuously tunable dye laser (360–900 nm) excitation source which has a

500 ps pulse width and an average energy of 240 μ J per pulse. The luminescence is detected at a right-angle to the excitation source and is passed through a PTI 01-001 monochromator for wavelength selection and is detected by a Hamamatsu R928 red-sensitive thermoelectrically cooled photomultiplier tube. The signal is digitized by a LeCroy 6880 fast digitizer and transferred to an IBM compatible computer for data handling and manipulation. The lifetime of the excited state was determined by a fit of the data to a single exponential function after eliminating the initial portion of the data which included the optical delay and the rise time of the photomultiplier tube.

Electrochemistry

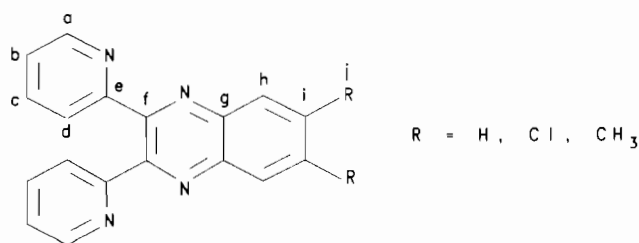
Cyclic voltammograms were recorded on a Bio-Analytical Systems 100A electrochemical analyzer equipped with a Houston Instruments DMP-40 digital plotter. The three-electrode system consisted of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver/silver chloride gel reference electrode (0.286 V versus NHE). The solvent used was Burdick and Jackson high-purity acetonitrile dried over activated molecular sieves. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. The solutions were deoxygenated by bubbling with argon for 20 min prior to each scan and blanketed with argon during the scan. The glassy-carbon working electrode was manually cleaned prior to each individual scan. Peak potentials were reproducible to within ± 0.02 V.

NMR spectroscopy

The NMR spectra of the free ligands were obtained on a Varian Unity-500 spectrometer operating at 125.7 (^{13}C) MHz. Each sample was dissolved in $CDCl_3$, and all reported chemical shifts are versus $CDCl_3$.

Results and discussion

The identity of Cl_2dpq and Me_2dpq was established by ^{13}C NMR spectroscopy. Shown below is a representation of the bridging ligands showing the labels used for each carbon in the assignment of the ^{13}C NMR spectra.



The ^{13}C NMR chemical shifts, as well as our assignments, are shown in Table 1. The unsubstituted dpq ligand is included for comparison. Our assignments of the ^{13}C spectrum of the unsubstituted dpq ligand are in agreement with those of Murphy and co-workers [3c]. In contrast to their results, we were able to observe resonances for all carbons, including the bridgehead carbons with no hydrogens attached. The assignments of the ^{13}C spectra of Cl_2dpq and Me_2dpq are made by analogy to the unsubstituted dpq spectra. As expected, the peak corresponding to C(i) is shifted downfield in both the Cl_2dpq and Me_2dpq NMR spectra. Further NMR experiments will be conducted in an attempt to verify the ^{13}C assignments.

The cyclic voltammetric data for the free ligands Cl_2dpq , Me_2dpq , dpp, dpq and dpb [4, 5] are given in Table 2. As expected the substitution of the two electron donating methyl groups on the dpq framework in Me_2dpq results in a ligand which is harder to reduce than dpq. The substitution of the electron withdrawing chloro groups on the dpq framework results in a ligand, Cl_2dpq , which is easier to reduce than unsubstituted dpq. This yields a series of chelating polypyridyl bridging ligands with π^* orbitals varying in energy by 0.66 V, as determined by cyclic voltammetry, with $\text{dpp} > \text{Me}_2\text{dpq} > \text{dpq} > \text{Cl}_2\text{dpq} > \text{dpb}$.

Incorporation of these substituted dpq ligands into monometallic and bimetallic ruthenium bipyridine sys-

TABLE 1. ^{13}C chemical shifts (ppm) and assignments for dpq, Me_2dpq and Cl_2dpq

Carbon	Chemical shift (ppm)		
	dpq	Cl_2dpq	Me_2dpq
a	148.6	148.6	148.6
b	123.0	123.3	122.8
c	136.7	136.8	136.7
d	124.2	124.2	124.2
e	152.5	153.5	151.5
f	157.4	156.9	157.7
g	141.1	139.9	140.1
h	130.5	130.0	128.4
i	120.4	135.1	141.2
j			20.5

TABLE 2. Cyclic voltammetric data for a series of polypyridyl bridging ligands

Ligand	$E_{1/2}$
dpp	-1.80
Me_2dpq	-1.55
dpq	-1.43
Cl_2dpq	-1.18
dpb	-1.14

tems has been accomplished. The cyclic voltammetric data of the metal complexes $[(\text{bpy})_2\text{Ru}(\text{BL})]^{2+}$ and $\{[(\text{bpy})_2\text{Ru}]_2(\text{BL})\}^{4+}$ (where $\text{BL} = \text{Me}_2\text{dpq}$ and Cl_2dpq) along with the previously prepared dpp, dpq and dpb systems [5] are summarized in Tables 3 and 4. Although the electrochemistry for the dpp, dpq and dpb ruthenium complexes has been previously reported [3, 5], $E_{1/2}$ values vary significantly. Therefore, all electrochemical data reported herein were measured under our conditions. The monometallic systems exhibit one reversible oxidation and three reversible reductions within the solvent window ($i_p^a/i_p^c = 1$). By analogy to the unsubstituted dpq complex, $[\text{Ru}(\text{bpy})_2(\text{dpq})]^{2+}$, the oxidative process can be assigned as an Ru(II)/Ru(III) couple and is reversible on the cyclic voltammetric time scale [5]. The metal becomes slightly harder to oxidize for bridging ligands that are easier to reduce. This shift in the metal oxidation potential is due to an increase in the electron withdrawing ability of the bridging ligands with $\text{dpp} < \text{Me}_2\text{dpq} < \text{dpq} < \text{Cl}_2\text{dpq} < \text{dpb}$. The three reductions correspond to sequential one electron reductions of the polypyridyl ligands with the first reduction

TABLE 3. Cyclic voltammetric data for a series of ruthenium monometallic bipyridyl complexes containing polypyridyl bridging ligands

Complex	Reductions			
	$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)
$[\text{Ru}(\text{bpy})_3]^{2+ \text{ a}}$	1.31	-1.30	-1.49	-1.72
$[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+ \text{ b}}$	1.38	-1.01	-1.46	-1.67
$[\text{Ru}(\text{bpy})_2(\text{Me}_2\text{dpq})]^{2+}$	1.40	-0.84	-1.43	-1.64
$[\text{Ru}(\text{bpy})_2(\text{dpq})]^{2+ \text{ b}}$	1.47	-0.72	-1.40	-1.62
$[\text{Ru}(\text{bpy})_2(\text{Cl}_2\text{dpq})]^{2+}$	1.48	-0.63	-1.32	-1.62
$[\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+ \text{ b}}$	1.48	-0.62	-1.26	-1.60

^aRef. 1. ^bAlthough these complexes have been previously prepared (refs. 3 and 5) this data is using complexes prepared and studied under our conditions for comparison.

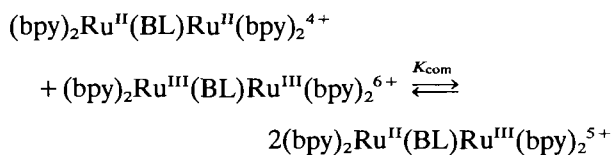
TABLE 4. Cyclic voltammetric data for a series of ruthenium bimetallic bipyridyl complexes containing polypyridyl bridging ligands

Complex	Oxidations		Reductions	
	$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)
$\{[(\text{bpy})_2\text{Ru}]_2(\text{dpp})\}^{4+ \text{ a}}$	1.43	1.61	-0.61	-1.09
$\{[(\text{bpy})_2\text{Ru}]_2(\text{Me}_2\text{dpq})\}^{4+}$	1.48	1.65	-0.41	-1.15
$\{[(\text{bpy})_2\text{Ru}]_2(\text{dpq})\}^{4+ \text{ a}}$	1.52	1.67	-0.32	-1.10
$\{[(\text{bpy})_2\text{Ru}]_2(\text{Cl}_2\text{dpq})\}^{4+}$	1.53	1.72	-0.20	-0.89
$\{[(\text{bpy})_2\text{Ru}]_2(\text{dpb})\}^{4+ \text{ a}}$	1.52	1.70	-0.22	-0.87

^aAlthough these complexes have been previously prepared (refs. 3 and 5) this data is on complexes prepared and studied under our conditions for comparison.

corresponding to the BL/BL⁻ couple [3, 5]. Since both Me₂dpq and Cl₂dpq as the free ligands reduce at lower potential than bpy, it is anticipated that the first reduction on the metal complexes will correspond to a bridging ligand based reduction. This bridging ligand based reduction shifts significantly to more positive potential as a function of bridging ligand with dpp < Me₂dpq < dpq < Cl₂dpq < dpb. The second and third reductions which are bipyridine based couples, bpy/bpy⁻, also shift to more positive potentials as the easier to reduce bridging ligands are substituted into the Ru^{II}(bpy)₂ framework. The magnitude of this shift is much less than the shift observed for the bridging based reductions. This shift is most likely due to the indirect effect of the increase in positive charge on the metal center caused by the increase in electron withdrawing ability of the bridging ligands. In these monometallic systems the highest-occupied molecular orbital (HOMO) is a ruthenium based dπ orbital and the LUMO is a bridging ligand based π* orbital [5].

The electrochemical data for the bimetallic systems is given in Table 4. The bimetallic systems exhibit two oxidations and four reductions in the solvent window. The half wave potentials for both oxidations and the first two reductions are also given in Table 4. The two oxidative processes correspond to sequential one electron oxidations of the two ruthenium centers from Ru(II) to Ru(III) [3, 5]. As seen in the monometallic complexes the metal becomes somewhat harder to oxidize as the more electron withdrawing bridging ligands are substituted into the {[bpy]₂Ru₂(BL)}⁴⁺ framework. The two equivalent metal centers oxidize at different potentials since they are electronically coupled through the bridging ligand. The separation between these two oxidative waves is a measure of the increased stability of the mixed-valence form versus the two isovalent species [7]. Using this separation we can calculate the comproportionation constant, K_{com}.



The separation between the two oxidative waves and the comproportionation constants for this series of bimetallic systems are listed in Table 5. All of these complexes have fairly similar comproportionation constants indicating a stabilization of the mixed-valence systems.

The first two reductive processes in the bimetallic systems correspond to sequential reductions of the bridging ligand with the first reduction being the BL/BL⁻ couple and the second the BL⁻/BL²⁻ couple. The presence of two bridging ligand based reductions

TABLE 5. Comproportionation constants for a series of ruthenium bimetallic bipyridyl complexes containing polypyridyl bridging ligands

Complex	$\Delta E_{1/2}$ (mV)	K_{com}
{[(bpy) ₂ Ru] ₂ (dpp)} ⁴⁺ ^a	180	1.1 × 10 ³
{[(bpy) ₂ Ru] ₂ (Me ₂ dpq)} ⁴⁺	170	7.5 × 10 ²
{[(bpy) ₂ Ru] ₂ (dpq)} ⁴⁺ ^a	150	3.4 × 10 ²
{[(bpy) ₂ Ru] ₂ (Cl ₂ dpq)} ⁴⁺	190	1.6 × 10 ³
{[(bpy) ₂ Ru] ₂ (dpb)} ⁴⁺ ^a	180	1.1 × 10 ³

^aAlthough these complexes have been previously prepared (refs. 3 and 5) this data is on complexes prepared and studied under our conditions for comparison.

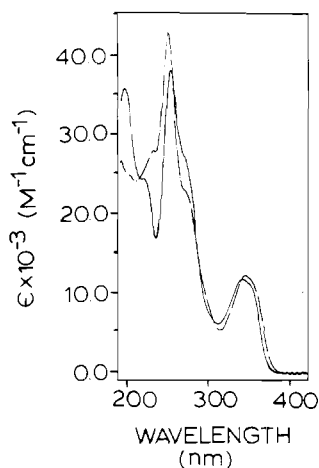


Fig. 1. Electronic absorption spectra for Cl₂dpq (---) and Me₂dpq (—).

prior to the bipyridine based reductions has previously been attributed to a lowering of the energy of the π* orbital on the bridging ligand significantly below the energy of the bipyridine based π* orbital by the simultaneous coordination of the two positive metal centers of the bridging ligand [5]. As expected both reduction potentials shift to more positive potential as the bridging ligand becomes easier to reduce within the series. As in the monometallic systems, these bimetallic complexes have a ruthenium based dπ HOMO and a bridging ligand based π* LUMO. As seen in the electrochemical data the magnitude of the shift of the HOMO is much less than that of the LUMO. Thus, through the systematic variation of the bridging ligand from dpp to Me₂dpq, dpq, Cl₂dpq and dpb it is possible to significantly shift the energy of the bridging ligand based π* orbital while maintaining a fairly constant ruthenium based (dπ) HOMO.

The relative energy of the lowest lying excited states in these systems is dominated by the shift in the bridging ligand based π* LUMO. The electronic spectra of Me₂dpq and Cl₂dpq are shown in Fig. 1. The energy of the lowest lying π → π* transitions and the energy

of the emissions for the free bridging ligands are given in Table 6. A shift to lower energy in both the absorption and emission in these systems is observed with $\text{dpp} > \text{Me}_2\text{dpq} > \text{dpq} > \text{Cl}_2\text{dpq} > \text{dpb}$. This shift is similar to that observed for the reduction potentials of the free ligands and is most likely due to a stabilization of the π^* orbital.

The electronic spectra for the newly prepared monometallic complexes are shown in Fig. 2 and the electronic spectral data for the ruthenium monometallic systems including the absorption maxima for the lowest energy transition as well as the emission energy and excited state lifetime are summarized in Table 7 [5]. Since the substitution of the bridging ligands from dpp to Me_2dpq , dpq, Cl_2dpq and dpb give systems with lower lying bridging ligand based π^* LUMOs and fairly constant ruthenium based HOMOs, the energy gap between the HOMO and LUMO should decrease from dpp to Me_2dpq , dpq, Cl_2dpq and dpb. The energy of the $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}(\pi^*)\text{MLCT}$ absorption and emission decreases in accord with this expectation on going from the dpp to Me_2dpq , dpq, Cl_2dpq and dpb based complexes. As the energy of the emissive state decreases, the lifetime of that excited state also decreases with

TABLE 6. Electronic spectral data for a series of polypyridyl bridging ligands

Ligand	λ_{max} (nm)	
	Absorption	Emission
dpp ^a	284	402
Me_2dpq	341	404
dpq ^a	332	410
Cl_2dpq	354	411
dpb ^a	378	492

^aRefs. 4 and 5.

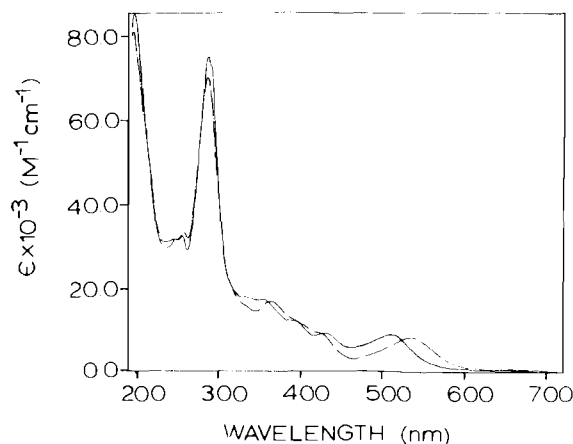


Fig. 2. Electronic absorption spectra for $[(\text{bpy})_2\text{Ru}(\text{Cl}_2\text{dpq})]^{2+}$ (---) and $[(\text{bpy})_2\text{Ru}(\text{Me}_2\text{dpq})]^{2+}$ (—) in acetonitrile at room temperature.

TABLE 7. Electronic spectral data for a series of ruthenium monometallic bipyridyl complexes containing polypyridyl bridging ligands

Complex	λ_{max} (nm)		τ (ns)
	Absorption	Emission	
$[\text{Ru}(\text{bpy})_3]^{2+}$ ^a	450	603	850
$[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ ^b	464	660	226
$[\text{Ru}(\text{bpy})_2(\text{Me}_2\text{dpq})]^{2+}$	508	750	19
$[\text{Ru}(\text{bpy})_2(\text{dpq})]^{2+}$ ^b	517	766	71
$[\text{Ru}(\text{bpy})_2(\text{Cl}_2\text{dpq})]^{2+}$	534	800	13
$[\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+}$ ^b	550	810	63

^aRef. 1. ^bRefs. 3 and 5.

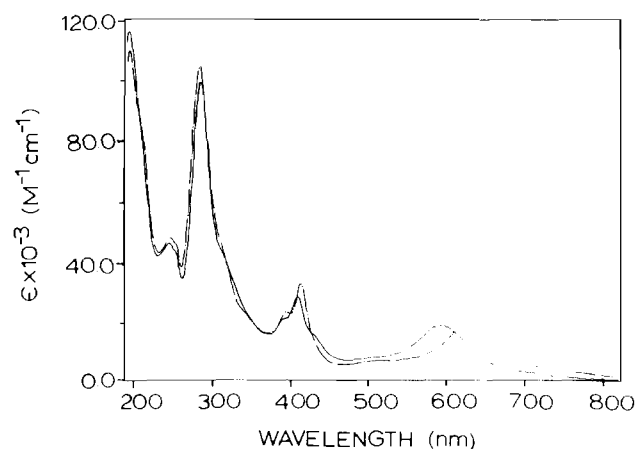


Fig. 3. Electronic absorption spectra for $[(\text{bpy})_2\text{Ru}_2(\text{Cl}_2\text{dpq})]^{4+}$ (---) and $[(\text{bpy})_2\text{Ru}_2(\text{Me}_2\text{dpq})]^{4+}$ (—) in acetonitrile at room temperature.

the Me_2dpq and Cl_2dpq complexes having somewhat shorter lifetimes. Although the introduction of the bridging ligands gives rise to a much shorter lifetime than $[\text{Ru}(\text{bpy})_3]^{2+}$, the presence of the remote nitrogens on the bridging ligands makes possible the covalent attachment of an additional metal center. Thus, the 10–20 ns lifetimes typical of the bridging ligand systems should be sufficient for intramolecular photosensitization.

The electronic spectra for the Cl_2dpq and Me_2dpq bridged bimetallic systems are shown in Fig. 3 and the electronic spectral data for the bimetallic complexes are summarized in Table 8. The coordination of the second metal center to the remote nitrogens on the bridging ligand to form the bimetallic system results in a further stabilization of the π^* orbital, as evidenced by the reduction potentials. This results in a decreased HOMO to LUMO gap and gives rise to lower energy transitions in the bimetallic systems as compared to the monometallic analogues. Within the series of bimetallic complexes, the lowest energy $\text{Ru} \rightarrow \text{BL}$ MLCT transition shifts to lower energy as easier to reduce

TABLE 8. Electronic spectral data for a series of ruthenium bimetallic bipyridyl complexes containing polypyridyl bridging ligands

Complex	λ_{\max} (nm)	
	Absorption	Emission
$\{[(bpy)_2Ru]_2(dpp)\}^{4+}$ ^a	525	755
$\{[(bpy)_2Ru]_2(Me_2dpq)\}^{4+}$	593	808
$\{[(bpy)_2Ru]_2(dpq)\}^{4+}$ ^a	603	822
$\{[(bpy)_2Ru]_2(Cl_2dpq)\}^{4+}$	635	860
$\{[(bpy)_2Ru]_2(dpb)\}^{4+}$ ^a	644	

^aRefs. 3 and 5.

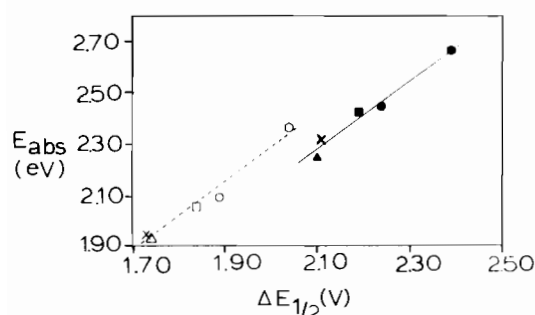


Fig. 4. Plot of energies of the lowest energy absorption band (eV) vs. $\Delta E_{1/2}$ (V) of $[(bpy)_2Ru(BL)]^{2+}$ with BL = dpp (○), Me_2dpq (●), dpq (■), Cl_2dpq (×), dpb (▲) and $\{[(bpy)_2Ru]_2(BL)\}^{4+}$ with BL = dpp (○), Me_2dpq (○), dpq (□), Cl_2dpq (×), dpb (△).

bridging ligands are introduced with the energy of the MLCT decreasing in the order $dpp > Me_2dpq > dpq > Cl_2dpq > dpb$ bimetallics. The emission of $\{[(bpy)_2Ru]_2(dpb)\}^{4+}$ is expected to occur in the near-IR region of the spectrum and is beyond the detection limits of our fluorometer and therefore no emission maximum is reported.

As noticed by other authors [5, 8], a correlation can be drawn between the electrochemical energy gap and the spectroscopic energy gap within a series of similar complexes. If the electrochemical processes, i.e. the metal based oxidation and the bridging ligand based reduction, correspond to the same orbitals involved in the spectroscopic transition, i.e. $Ru(d\pi) \rightarrow BL(\pi^*)$ MLCT, one would expect that a plot of these two measures of the energy gap between the HOMO and LUMO would show a correlation. Shown in Fig. 4 is a plot of $\Delta E_{1/2}$ versus $E_{abs}(MLCT)$ for the mono- and bimetallic systems (where $\Delta E_{1/2} = E_{1/2}(Ru^{II}/Ru^{III}) - E_{1/2}(BL/BL^-)$). Both sets of data give reasonably straight lines with correlation coefficients of 0.987 and 0.985 for the mono- and bimetallic systems, respectively. It is interesting to note that the slope of both lines are the same while the y-intercept for the monometallic systems is considerably less than for the bimetallic complexes. The electrochemical and spectroscopic meas-

ures of the energy gap between the $Ru(d\pi)$ HOMO and the $BL(\pi^*)$ LUMO do not give the same value. This is due in part to the fact that the optical transition occurs without time for the internuclear distances to rearrange to accommodate the new electronic configuration or the electron spin to flip. This results in a spectroscopic energy gap which is greater than the electrochemical energy gap. This difference in the two measures of the energy gap gives rise to a non-zero y-intercept of the plot of $\Delta E_{1/2}$ versus $E_{abs}(MLCT)$. Therefore, the difference in the intercept for the mono- and bimetallic systems is consistent with the fact that the bimetallic system contains more nuclei coordinated to the bridging ligand and might therefore be expected to undergo a larger degree of nuclear rearrangement in order to accommodate the new electronic configuration of the excited state.

Through the introduction of substituent groups on the dpq framework, it has been possible to tune the energy of the π^* orbital on these polypyridyl bridging ligands. It is this bridging ligand based π^* orbital that is occupied in the lowest lying excited state and first electrochemical reduction for either the monometallic or bimetallic complexes, $[(bpy)_2Ru(BL)]^{2+}$ or $\{[(bpy)_2Ru]_2(BL)\}^{4+}$. Therefore, through the variation of the nature of these substituents it is possible to fine tune the energy of the excited state of polymetallic systems. Through the further utilization of this substituent approach on dpp, dpq and dpb, it should be possible to prepare a large series of similar bridging ligands with widely varied π^* orbital energies [9]. Incorporation of this series of bridging ligands into a variety of multimetallic systems should be quite useful in studying and tuning the complex spectroscopy and electrochemistry of supramolecular systems.

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