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Laser Flash Photolysis and Pulse Radiolysis Studies of Ruthenium Complexes

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The absorption spectra of charge-transfer excited states and one-electron-reduced states of a number of mono- and binuclear ruthenium complexes in water have been obtained using laser flash photolysis and pulse radiolysis techniques. For Ru(dhp)$_3^{+*}$, the absorption bands are assigned by comparison with Ru(bpy)$_3^{+*}$. The spectra obtained for Ru(dpp)$_3^{+*}$ and Ru(dpq)$_3^{+*}$ are similar to their respective ground-state absorption spectra. Bimolecular rate constants for the reaction of e_{aq} with the above complexes as well as with the mixed-ligand complexes Ru(bpy)$_2$dpp^{2+} and Ru(bpy)$_2$dhp^{2+}, were also determined. From their characteristic absorption spectra and the bimolecular rate constants, it was concluded that the added electron is localized on one of the ligands. The excited-state absorption spectra of the two mixed-ligand complexes showed bands at 360 and 450 nm attributed to π–π^* transitions of the ligand anion radical. The lifetimes of the excited states of the complexes decreased on changing the solvent from acetonitrile to water. It was also observed that the lifetimes of the excited states of the binuclear complexes were shorter than those of the corresponding mononuclear complexes.

Introduction

The relatively long lifetime of the charge-transfer excited state of the ruthenium(II) polypyridine complex and its favorable redox properties have led to extensive studies of such complexes. Much of the interest has concerned photophysical, photochemical, electrochemical, and chemiluminescence studies (for a recent review, see ref 1). As a basis for the interpretation of the solution absorption spectra of Ru(bpy)$_3^{2+*}$ (the luminescent state) and related species such as Ru(bpy)$_3^{+}$, it is essential to be able to interpret and assign the absorption bands of Ru(bpy)$_3^{2+}$ itself. The principal bands in the absorption spectrum of Ru(bpy)$_3^{2+}$ at 285 and 450 nm have been assigned to singlet LC π–π^* and dπ–π^* MLCT transitions, respectively.[2–6] For the one-electron-reduced species in DMSO, Ru(bpy)$_3^{+}$, these two sets of transitions are observed at 292 nm (LC π–π^*) and 474 nm (MLCT dπ–π^*), respectively.[7] In addition, there are extra bands at 342, 502, 529, 780, 870, and 990 nm which are assigned to LC π–π^* transitions of coordinated bpy$^-$.[7] In the case of free, uncoordinated bpy$^-$ in THF solution, there are corresponding LC π–π^* transitions at 386, 532, 562, 751, 833, and 952 nm.[7,8] Only one of these transitions is observed in aqueous solution.[9] The luminescent state of Ru(bpy)$_3^{2+}$ (Ru(bpy)$_3^{2+*}$) arises from a MLCT transition and is mainly triplet in character, the quantum yield for intersystem crossing being unity (see ref 1). The most well-resolved absorption spectrum of this state has been recorded by Braterman *et al.*[6] In aqueous solution, five intense bands are observed at 250, 320, 376, 444, and 541 nm, assigned as LC π–π^* (bpy and bpy$^-$), LC π–π^* (bpy), LC π–π^* (bpy$^-$), MLCT (Ru(III)) dπ–π^* + LC π–π^* (bpy$^-$), and LC π–π^* (bpy$^-$), respectively. It should be noted that the familiar MLCT transition observed for Ru(bpy)$_3^{2+}$ itself is not observed or expected from Ru(bpy)$_3^{2+*}$ since the ruthenium ion is formally in the 3+ oxidation state. From such comparisons, it has been established that there are obvious similarities between the spectrum of Ru(bpy)$_3^{2+*}$ and those of bpy, bpy$^-$, and Ru(bpy)$_3^{+}$, which, taken together, support the view that the excited electron in the MLCT transition is localized on one bipyridine ligand (see ref 1 and refs 10–12). More substantial proof that the electron is localized on the ligand has come from Raman measurements on both the excited and one-electron-reduced states of ruthenium(II) complexes.[12]

In recent years, there has been increasing interest in binuclear complexes of ruthenium,[13–18] which upon optical excitation provide a means of studying long-range interactions between the molecular components and also a basis for the development of supramolecular photochemistry. Much of the interest so far has concerned the use of 2,3-bis(2-pyridyl)pyrazine (dpp) as the bridging ligand with 2,2′-bipyridine (bpy) as "spectator ligand".

In this study, laser flash photolysis and pulse radiolysis techniques have been applied to record and assign the absorption bands of the excited states (MLCT) and one-electron-reduced states of some mononuclear and binuclear ruthenium(II) complexes. The bridging ligands used were dpp and dhp (see Chart 1 for ligand structures), and the specific complexes were Ru-

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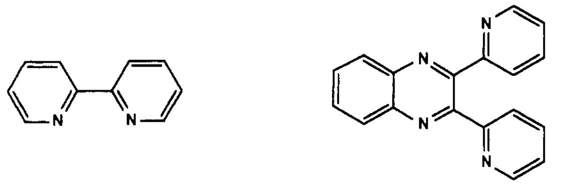
Chart 1. Structures of the Ligands Used in This Study

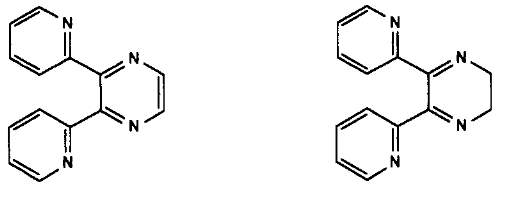


2,2'-bipyridine

(bpy)

2,3-bis(2-pyridyl)-quinoxaline

(dpq)



2,3-bis(2-pyridyl) pyrazine

(dpp)

2,3-bis(2-pyridyl)-5,6-dihydropyrazine

(dhp)

$(dhp)_3{}^{2+}$, $Ru(dpq)_3{}^{2+}$, $Ru(dpp)_3{}^{2+}$, $Ru(bpy)_2dpp^{2+}$, $Ru(bpy)_2dhp^{2+}$, $Ru(bpy)_2dhpRu(bpy)_2{}^{4+}$, and $Ru(bpy)_2dppRu(bpy)_2{}^{4+}$. The one-electron-reduction potentials of 2,2'-bipyridine (bpy), 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)-5,6-dihydropyrazine (dhp), and 2,3-bis(2-pyridyl)quinoxaline (dpq) are −2.21, −1.90, −1.76, and −1.56 V, respectively.[28] Some transient absorption spectra have previously been recorded for the mono- and binuclear dpp complexes.[13] Some of these were recorded in CH_2Cl_2 solutions and only difference spectra were presented, making assignments of bands difficult if not impossible.[13] In another study, the spectra were recorded in ethanolic solutions using high-energy laser pulses in attempts to completely convert the ground-state complex to the MLCT excited state.[16] For the one-electron-reduced species, cyclic voltammetry in DMF solution has been used in previous studies to produce the one-electron-reduced form of the dpp mono- and binuclear complexes.[16] In this work, fully corrected transient absorption spectra of the excited MLCT states of the complexes are presented using a comparative method employing relatively low energy laser pulses, thus decreasing the possibility of multiphoton absorption. For the one-electron-reduced states of both the ligand and complexes, the technique of pulse radiolysis allows spectral measurement in aqueous solution, thus enabling direct comparison with those excited-state spectra recorded also in aqueous solution.

Experimental Section

Samples of $Ru(dhp)_3{}^{2+}$, $Ru(dpp)_3{}^{2+}$, $Ru(dpq)_3{}^{2+}$, $Ru(bpy)_2dpp^{2+}$, $Ru(bpy)_2dhp^{2+}$, $Ru(bpy)_2dhpRu(bpy)_2{}^{4+}$, and $Ru(bpy)_2dppRu(bpy)_2{}^{4+}$ were prepared by synthetic routes previously published.[19–21] All solvents were of spectroscopic grade and were used as received. Water was either triply distilled (the last distillation being over $KMnO_4$) or purified by passage through a Millipore filtration system. Solutions were in free equilibrium with air or were purged with nitrogen or oxygen as appropriate. All experiments were conducted at ambient temperature (22 ± 2 °C). All laser flash photolysis experiments involving $Ru(dhp)_3{}^{2+}$ and $Ru(dpp)_3{}^{2+}$ were performed at The North East Wales Institute. Laser flash photolyses of $Ru(dpq)_3{}^{2+}$, $Ru(bpy)_2dpp^{2+}$, $Ru(bpy)_2dhp^{2+}$, $Ru(bpy)_2dhpRu(bpy)_2{}^{4+}$, and $Ru(bpy)_2dppRu(bpy)_2{}^{4+}$ were performed at the Center for Fast Kinetics Research (Austin, TX). Experiments on the latter four compounds were also carried out at Yarmouk University.

The laser flash photolysis system at The North East Wales Institute consists of a pulsed excitation source (JK System 2000 Nd:YAG laser with a pulse width of 12 ns) from which the second (532 nm) or third (353 nm) harmonic was selected.[22] Transient absorption was monitored using a pulsed xenon arc lamp, monochromator, and RCA IP28 photomultiplier tube. A Phillips 3311 digital oscilloscope coupled to a Hewlett Packard microcomputer was used for data analysis. For luminescence measurements, the second harmonic was exclusively used, luminescence being detected perpendicular to the excitation beam. Laser energy, unless otherwise stated, was approximately 1 mJ/pulse to avoid biphotonic effects.

The laser flash photolysis experiments at the Center for Fast Kinetics Research were carried out using the second or third harmonic (532 or 355 nm, respectively) from a Quantel YG 4023 Nd:YAG laser system (pulse width 300 ps). For absorption experiments, the detection system comprised a pulsed xenon arc lamp, monochromator, and photomultiplier tube (Hamamatsu R928). Output waveforms were digitized using a Tektronix R7912 transient digitizer interfaced to an on-line DEC PDP 11/70 computer for data analysis. Laser energy was approximately 1 mJ/pulse. For luminescence experiments, the second harmonic was exclusively used. The laser flash photolysis experiments carried out at the University of Yarmouk employed an Applied Photophysics K347 laser flash spectrometer in absorption mode with excitation from a Spectron Nd:YAG laser at 355 nm. All laser experiments employed a path length of 1 cm.

All pulse radiolysis studies were carried out at the Paterson Institute for Cancer Research, Manchester, U.K. The pulse radiolysis experiments were carried out with an 8–14-MeV Vickers electron linear accelerator (pulse lengths 5–50 ns) as previously described.[23] Typical experiments employed 10- and 20-ns pulses (dose in range 1–10 Gy/pulse). Optical cells of path length 2.5 cm were used. Radiation doses were measured using the absorption of $(SCN)_2{}^{\bullet-}$ formed by pulsing nitrous oxide saturated solutions of 10^{-2} mol dm^{-3} KSCN taking $G[(SCN)_2{}^{\bullet-}] = 0.61\ \mu\text{mol J}^{-1}$ and $\epsilon[(SCN)_2{}^{\bullet-}](480\text{ nm}) = 7730\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$.

All solutions, in both laser flash photolysis and pulse radiolysis experiments, were purged with either nitrogen, nitrous oxide, or oxygen for at least 30 min before excitation. Moreover, fresh solutions were used for each shot using a flow system.

Results

The difference transient absorption spectra of $Ru(dhp)_3{}^{2+*}$, $Ru(dpq)_3{}^{2+*}$, and $Ru(dpp)_3{}^{2+*}$ were recorded (*ca.* 8 ns) following pulsed laser excitation of nitrogen-saturated solutions of the respective ruthenium complex at 355 nm and are shown in Figures 1–3. Correction of these spectra for loss of ground-state absorption was carried out by comparing the experimental transient absorbance at 360 nm of these complexes with that of $Ru(bpy)_3{}^{2+}$ using identical excitation conditions (i.e., both the $Ru(bpy)_3{}^{2+}$ solution and the solutions of the complexes studied have the same absorbance at 355 nm, the excitation wavelength). By taking the extinction coefficient for the absorption difference between the MLCT excited and ground states of $Ru(bpy)_3{}^{2+}$ to be -7.6×10^3 dm^3 mol^{-1} cm^{-1} at 450 nm (see ref 24), we could calculate the concentration of the MLCT state of $Ru(bpy)_3{}^{2+}$. This concentration value, within ±15%, was then taken to be the concentration of the MLCT states, the error limits being determined largely by the uncertainties in the $Ru(bpy)_3{}^{2+*}$ extinction coefficients and also the transient absorbance measurements. On the assumption that the quantum yield for intersystem crossing (ISC) is unity, as found for $Ru(bpy)_3{}^{2+}$ [24–26] and other ruthenium complexes,[27] the corrected spectra were then calculated and are shown in

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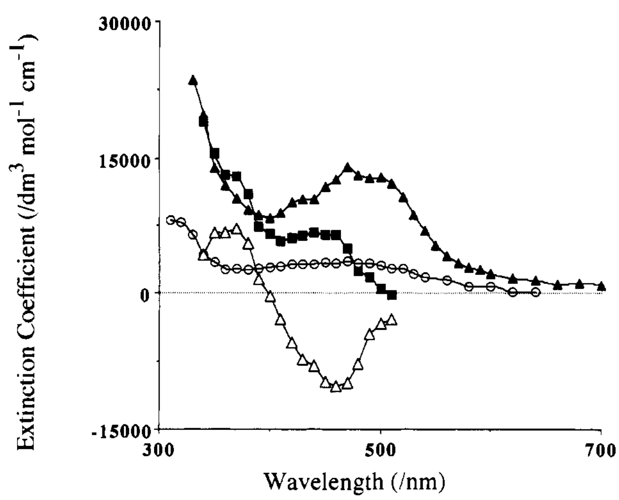

Figure 1. (i) Difference (△) and corrected (■) absorption spectra of $Ru(dhp)_3^{2+*}$ as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for $Ru(dhp)_3^+$ (▲) and $dhp^{•-}$ (○) as obtained using pulse radiolysis methods.

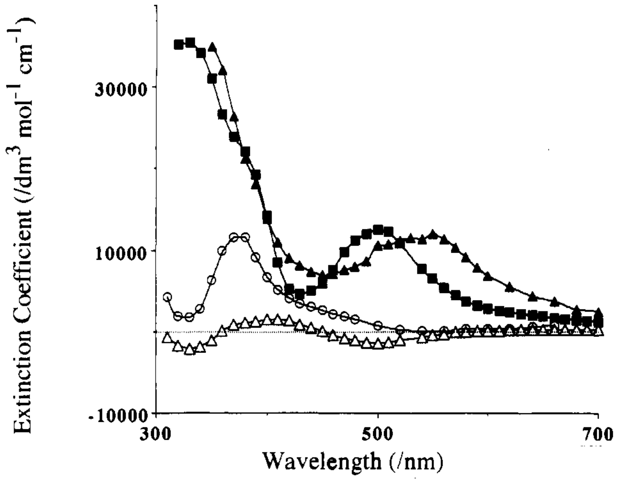

Figure 2. (i) Difference (△) and corrected (■) absorption spectra of $Ru(dpq)_3^{2+*}$ as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for $Ru(dpq)_3^+$ (▲) and $dpq^{•-}$ (○) as obtained using pulse radiolysis methods.

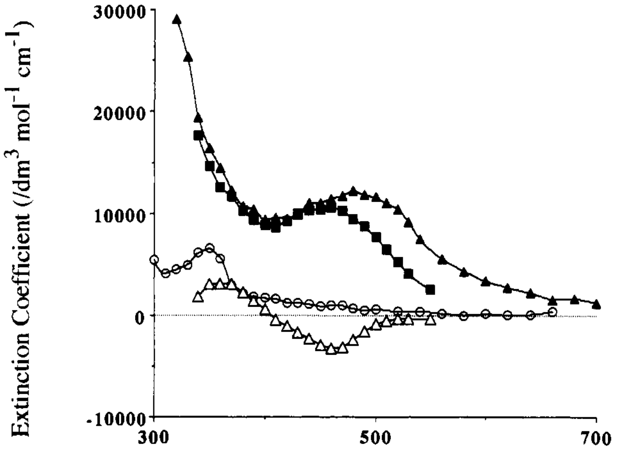

Figure 3. (i) Difference (△) and corrected (■) absorption spectra of $Ru(dpp)_3^{2+*}$ as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for $Ru(dpp)_3^+$ (▲) and $dpp^{•-}$ (○) as obtained using pulse radiolysis methods.

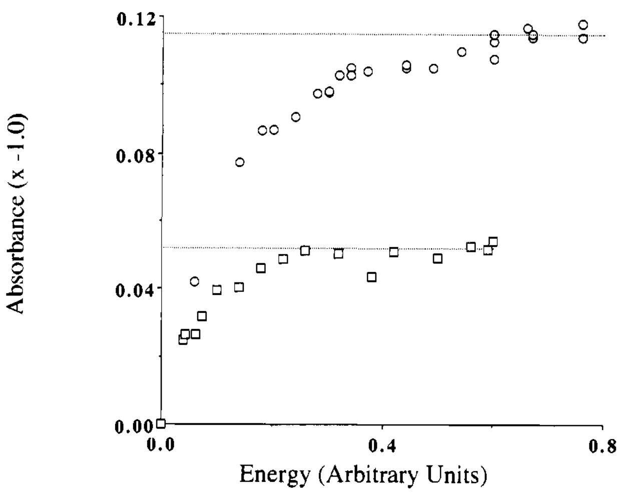

Figure 4. Effect of laser energy (abitrary units; $\lambda_{exc} = 532$ nm) on the transient MLCT absorption at 450 nm for aqueous solutions of $Ru(dhp)_3^{2+}$ (○, 1.2×10^{-5} mol dm^{-3}) and $Ru(dpp)_3^{2+}$ (□, 1.2×10^{-5} mol dm^{-3}).

Table 1. Bimolecular Rate Constants for Reactions of Ligands and Ru Complexes with the Hydrated Electron, e^-_{aq}, As Measured by Pulse Radiolysis Methods

species	$10^{-10}k$, dm^3 mol^{-1} s^{-1}	species	$10^{-10}k$, dm^3 mol^{-1} s^{-1}
dhp	2.4 ± 0.2	$Ru(dpq)_3^{2+}$	7.6 ± 0.7
dpp	2.4 ± 0.2	$Ru(bpy)_2dhp^{2+}$	6.5 ± 0.7
dpq	2.6 ± 0.3	$Ru(bpy)_2dpp^{2+}$	6.7 ± 0.7
$Ru(dhp)_3^{2+}$	7.8 ± 0.7	$Ru(bpy)_2dpp(bpy)_2Ru^{4+}$	9.3 ± 0.9
$Ru(dpp)_3^{2+}$	7.5 ± 0.7	$Ru(bpy)_2dhp(bpy)_2Ru^{4+}$	9.4 ± 0.9

Figures 1–3 for $Ru(dhp)_3^{2+*}$, $Ru(dpq)_3^{2+*}$, and $Ru(dpp)_3^{2+*}$, respectively. From the respective errors in the measurements of ground-state and excited-state absorptions, it was estimated that the largest errors in the measurement of the corrected spectra would be ±12% (460 nm), ±3% (500 nm), and ±9% (460 nm) for $Ru(dhp)_3^{2+}$, $Ru(dpq)_3^{2+*}$, and $Ru(dpp)_3^{2+*}$, respectively. In no case were the shapes or intensities of the corrected spectra significantly affected.

As an independent check for the correction of the difference transient absorption spectra, attempts were made to convert all of the ground states of the ruthenium complexes to the charge-transfer states by using high-power laser pulses. This was successful for $Ru(dhp)_3^{2+}$ and $Ru(dpp)_3^{2+}$ (see Figure 4). Extinction coefficients calculated from these experiments agreed closely (within 10%) with those calculated using $Ru(bpy)_3^{2+}$ as a standard. Also shown in Figures 1–3 (for the purpose of comparison) are the corrected transient absorption spectra of the ligand radical ions (or protonated forms) and of $Ru(dhp)_3^+$, $Ru(dpq)_3^+$, and $Ru(dpp)_3^+$. These latter species were produced in pulse radiolysis experiments using nitrogen-saturated solutions containing 0.1 mol dm^{-3} *tert*-butyl alcohol according to the following reactions (using dhp as an example):

$$H_2O \rightsquigarrow e^-_{aq}, {}^{•}OH, H^{•}, H_2, H_2O_2, H_3O^+ \qquad (1)$$

either

$$e^-_{aq} + dhp \rightarrow dhp^{•-} \qquad (2)$$

or

$$e^-_{aq} + Ru(dhp)_3^{2+} \rightarrow Ru(dhp)_3^+ \qquad (3)$$

The •OH radicals react with *tert*-butyl alcohol to give free radicals which are generally assumed to be unreactive. The yield of H• is small compared to that of e^-_{aq}, and its reactions have been ignored here. The pH values of the solutions were in the range 6–7 (unbuffered). The rates of reaction of e^-_{aq} with the various ruthenium complexes are given in Table 1. At the end of the decay of the e^-_{aq} absorption (generally <1 μs following the pulse), the spectra of the reduced species could be measured and corrected for loss of either ligand or ruthenium complex ground-state

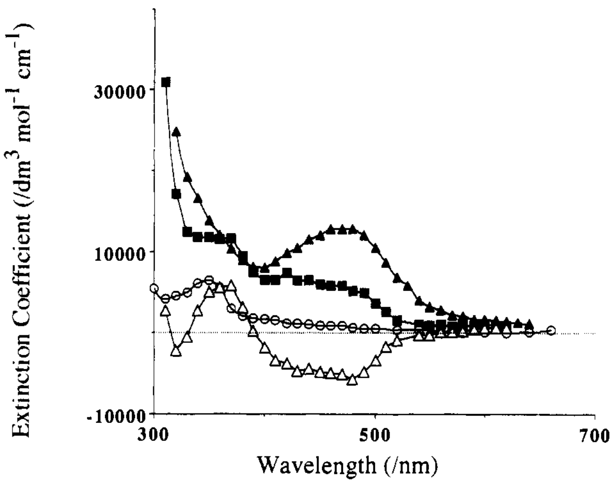

Figure 5. (i) Difference (△) and corrected (■) absorption spectra of Ru(bpy)$_2$dpp^{2+*} as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for Ru(bpy)$_2$dpp$^+$ (▲) and dpp$^{\bullet-}$ (○) as obtained using pulse radiolysis methods.

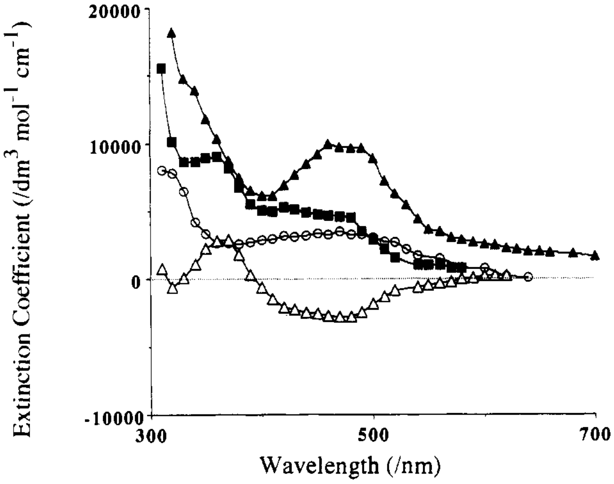

Figure 6. (i) Difference (△) and corrected (■) absorption spectra of Ru(bpy)$_2$dhp^{2+*} as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for Ru(bpy)$_2$dhp$^+$ (▲) and dhp$^{\bullet-}$ (○) as obtained using pulse radiolysis methods.

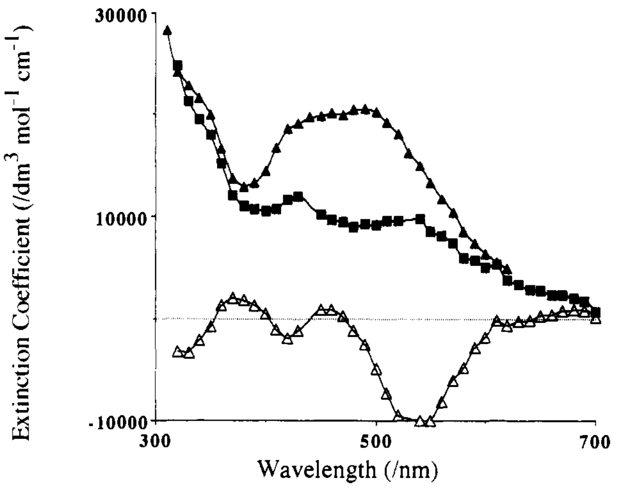

Figure 7. (i) Difference (△) and corrected (■) absorption spectra of Ru(bpy)$_2$dhp(bpy)$_2$Ru^{4+*} as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for Ru(bpy)$_2$dhp(bpy)$_2$Ru^{3+} (▲) as obtained using pulse radiolysis methods.

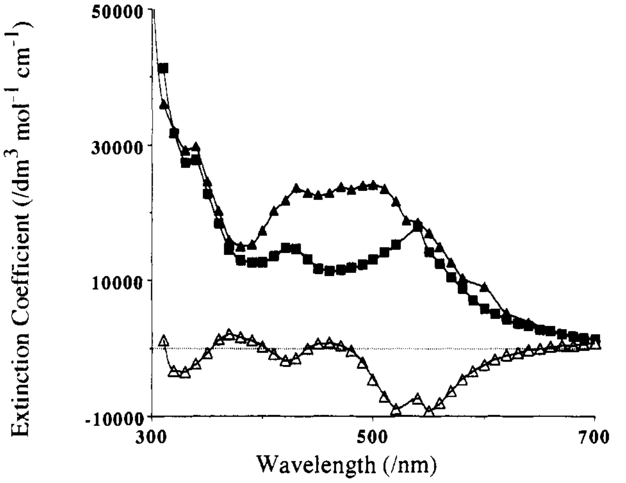

Figure 8. (i) Difference (▲) and corrected (■) absorption spectra of Ru(bpy)$_2$dpp(bpy)$_2$Ru^{4+*} as obtained by laser flash photolysis techniques. (ii) Corrected absorption spectra for Ru(bpy)$_2$dpp(bpy)$_2$Ru^{3+} (▲) as obtained using pulse radiolysis methods.

absorption by taking the yield of e^-_{aq} to be 0.28 μmol J^{-1}. The dose per pulse was in the range 5–10 Gy.

Identical laser flash photolysis experiments, described for tris complexes, were also carried out using the mixed-ligand complexes Ru(bpy)$_2$dpp^{2+} and Ru(bpy)$_2$dhp^{2+}. The excited-state transient uncorrected absorption spectra are shown in Figures 5 and 6.

As before, the corrected spectra were calculated by using the Ru(bpy)$_3$$^{2+*}$ absorption spectrum as a standard and by assuming unit ISC quantum yield. These spectra are also shown in Figures 5 and 6 and are compared as before with the spectra of the one-electron-reduced states and with the ligand free radical spectra.

The excited-state absorption spectra of some ruthenium binuclear complexes which contain the bridging ligands dhp and dpp have also been calculated by using the comparative technique and by assuming that the quantum yield for ISC is unity. Difference spectra are shown in Figures 7 and 8, from which the corrected spectra can be calculated (also shown in Figures 7 and 8). These latter spectra are compared, as before, with the spectra of the ligand free radicals and the one-electron-reduced states. From the respective errors in the measurements of the ground-state and excited-absorption spectra, it was estimated that the largest errors in the measurements of the corrected spectra would be ±15% (480 nm), ±10% (480 nm), ±15% (540 nm), and ±30% (540 nm) for Ru(bpy)$_2$dpp^{2+*}, Ru(bpy)$_2$dhp^{2+*}, Ru(bpy)$_2$dhp(bpy)$_2$Ru^{4+*}, and Ru(bpy)$_2$dpp(bpy)$_2$Ru^{4+*}, respectively. These error limits do not affect significantly the shapes of the spectra. Only for the last complex is there a significant effect on intensity, the effect being to sharpen or lengthen the long-wavelength tail of the spectrum. We also attempted complete conversion experiments for Ru(bpy)$_2$dhp(bpy)$_2$Ru^{4+} in acetonitrile. A plot (not shown) similar to that shown in Figure 4 was obtained where the difference absorbance at 550 nm was plotted against laser intensity. From that plot a value of 12 000 ± 1200 dm^3 mol^{-1} cm^{-1} was obtained for $\Delta\epsilon$ at 550 nm. Using the above value and benzophenone as a standard, the ISC for Ru(bpy)$_2$dpp(bpy)$_2$Ru^{4+} was calculated to be 0.9 ± 0.1.

The rate constants for the decays of the excited states (assumed to be ^{3}MLCT states) of the ruthenium complexes in this study were measured in nitrogen-saturated acetonitrile, water, and ethanol. Kinetic analysis, by both emission and absorption methods, yielded the decay constants (see Table 2) of the ^{3}MLCT states.

Discussion

The Tris Complexes. The ground-state spectrum of Ru(dhp)$_3$$^{2+}$ exhibits a maximum at 460 nm with a shoulder at about 430–440 nm. These peaks are similar to those of Ru(bpy)$_3$$^{2+}$ and Ru(dpp)$_3$$^{2+}$ at 455 nm, which have been assigned to MLCT transitions.[6,13,17] In view of the similarity in ligand structure of dhp and dpp to bpy, an identical assignment can be made here

Table 2. Rate Constnats for Decay (k) of the Charge-Transfer Excited States of Ruthenium Complexes[a]

complex	k, s^{-1}	k_q, dm^3 mol^{-1} s^{-1}	solvent	method
$Ru(dhp)_3^{2+}$	3.8×10^6	1.4×10^9	H_2O	emission
	5.0×10^6	6.0×10^8	MeCN	emission
	5.1×10^6	2.5×10^8	EtOH	emission
$Ru(dpp)_3^{2+}$	3.9×10^6	1.2×10^9	H_2O	emission
	6.4×10^6	4.4×10^8	MeCN	emission
	6.5×10^6	2.5×10^8	EtOH	emission
$Ru(dpq)_3^{2+}$	1.7×10^7	n.m.	H_2O	absorption
	2.3×10^7	n.m.	MeCN	absorption
	1.8×10^7	n.m.	EtOH	absorption
$Ru(bpy)_2dhp^{2+}$	7.3×10^6	2.2×10^9	H_2O	emission
	2.7×10^6	9.9×10^8	MeCN	emission
	5.1×10^6	4.0×10^8	EtOH	emission
$Ru(bpy)_2dpp^{2+}$	8.2×10^6	1.6×10^9	H_2O	emission
	2.7×10^6	1.0×10^9	MeCN	emission
	4.8×10^6	3.5×10^8	EtOH	emission
$Ru(bpy)_2dhp(bpy)_2Ru^{4+}$	2.1×10^7	n.m.	H_2O	absorption
	8.9×10^6	4.4×10^8	MeCN	absorption
	1.4×10^7	2.0×10^8	EtOH	absorption
$Ru(bpy)_2dpp(bpy)_2Ru^{4+}$	2.0×10^7	n.m.	H_2O	absorption
	9.3×10^6	4.9×10^8	MeCN	absorption
	1.4×10^7	1.6×10^8	EtOH	absorption

[a] The bimolecular rate constant for the reaction between the charge-transfer excited state and oxygen quenching (k_q) is shown. Errors in k and k_q are estimated at ±15% and ±25%, respectively.

for $Ru(dhp)_3^{2+}$. For $Ru(dpq)_3^{2+}$, the absorption spectrum shows instead a maximum at 500 nm, as observed for the dimethyl derivative, dbpq.[28] This band has been also assigned to an MLCT transition.[29] The dpq ligand contains an extended π-conjugated system, which would result in a lowering of the energies of the π orbitals of the dpq ligand and hence a red shift in its MLCT transition relative to those of the dpp, dhp, and bpy ligands.

The reduced forms of these three complexes, i.e. $Ru(dhp)_3^+$, $Ru(dpp)_3^+$, and $Ru(dpq)_3^+$, also exhibit characteristic spectra which are shown in Figures 1–3. All show three closely-spaced maxima which overlap with the MLCT transition of the unreduced state, the highest wavelength absorption band being some 40 nm red-shifted compared to the corresponding MLCT maxima in the ground state. The observations are consistent with those made for $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^+$ in aqueous solution where similar band structures and red shifts were found.[9] The shortest wavelength absorptions of these three maxima in $Ru(bpy)_3^+$ have been assigned to MLCT transitions (Ru → bpy^0) whereas the other two at slightly longer wavelength have been assigned to π–π^* transitions of coordinated bpy$^-$[6,7] (π_7–π_{10} using the nomenclature of Braterman *et al.*[6]). As for the MLCT transition observed for $Ru(dpq)_3^{2+}$, these three sets of transitions are red-shifted by about 40 nm relative to those of the dpp and dhp ligands, again reflecting the lower energies of the dpq π orbitals.

In characterizing the MLCT state of $Ru(bpy)_3^{2+}$, we have found the π–π^* transitions of bpy$^-$ in $Ru(bpy)_3^+$ and bpy$^-$ itself to be most useful.[6] In particular, the higher energy π–π^* transitions of bpy$^-$ (π_6–π_7[6]) at about 380 nm for $Ru(bpy)_3^{2+*}$ and bpy$^-$ have provided confirmation of the nature of the excited state. It would appear that the same transition in $Ru(bpy)_3^+$ is 20 nm blue-shifted and, therefore, is not so directly diagnostic. For $Ru(dhp)_3^{2+*}$ (Figure 1), there are bands at 370 nm (shoulder) and 440–460 nm. These bands are assigned to π–π^* transitions, π_6–π_7, and π_7–π_{11} transitions[6] associated with coordinated dhp$^-$. The ligand radical itself, dhp$^-$, shows a broad absorption (Figure 2) centered at 480 nm which overlaps the two π–π^* bands of coordinated dhp$^-$ in $Ru(dhp)_3^+$ at 480 and 510 nm and probably comprises the three bands π_6–π_7, π_7–π_{11}, and π_7–π_{10} expected at about 380, 460, and 550 nm, as for bpy$^-$. The absence of any maxima beyond about 500 nm for $Ru(dhp)_3^{2+*}$ probably reflects the difficulties associated with measuring absorption in a region where luminescence is also prominent. It thus seems reasonably clear that the absorption spectrum of $Ru(dhp)_3^{2+*}$ in Figure 1 represents a MLCT state in which a metal d electron is localized on the dhp ligand.

In the case of $Ru(dpp)_3^{2+*}$, the difference spectrum (Figure 1) shows relatively low extinction coefficients compared to those of the ground states (calculated assuming the ISC quantum yield is unity), and so it is not surprising that the corrected spectrum (Figure 3) of the excited state is similar to that of the ground state. As with $Ru(bpy)_3^{2+}$ and $Ru(dhp)_3^{2+}$, it might have been expected that the MLCT transitions in the ground state would have been twice as intense as the π_7–π_{11} transition in the excited state. However, laser energy saturation experiments support the difference extinction coefficients shown in Figures 1–3. It should be noted nevertheless that previous attempts to completely deplete the ground state of $Ru(bpy)_2dpp^{2+}$ resulted in 85% conversion.[16] In addition, there is some indication of increased absorption at 380 nm for the MLCT state relative to the ground state, providing some support for π–π absorptions of coordinated dpp$^-$.

For $Ru(dpq)_3^{2+}$ (Figure 2), the spectra are too similar to be able to justify any assignments based on a ligand-localized electron model. When the dpp and dpq ligands are reduced by e^-_{aq}, distinct absorption bands are seen at 350 and 370 nm, respectively. However, there is little characteristic absorption at higher wavelengths which may be used for comparison with the spectra of $Ru(dpp)_3^{2+}$, $Ru(dpq)_3^{2+*}$, $Ru(dpp)_3^+$, and $Ru(dpq)_3^+$. The characteristic bands of the reduced forms of the ruthenium complexes may, however, be taken to indicate that the unpaired electron is localized on the ligand. This is confirmed further by consideration of the bimolecular rate constants for the reaction between e^-_{aq} and the various complexes (Table 1). It appears the bimolecular rate increases linearly with the number of ligands in the complex, thus indicating that the initial attack of e^-_{aq} is on the ligand.

Mononuclear Mixed-Ligand Complexes. For mixed-ligand complexes, much attention has been paid to confirming the localization of the electron in the MLCT excited state on one or the other of the ligands. In this study, the UV/visible spectra of the two monomeric mixed complexes, $Ru(bpy)_2dpp^{2+}$ and $Ru(bpy)_2dhp^{2+}$ (see also Figures 5 and 6), appear to be consistent with "weighted average" spectra calculated from $Ru(bpy)_3^{2+}$, $Ru(dpp)_3^{2+}$, and $Ru(dhp)_3^{2+}$ spectra, confirming the existence of separate bpy, dhp, and dpp chromophoric systems. There are two bands apparent for both complexes, i.e. at about 420 and 480 nm. For $Ru(bpy)_2dpp^{2+}$, these have been attributed to Ru(II)–bpy and Ru(II)–dpp MLCT transitions, respectively.[13] An identical assignment is made here for the $Ru(bpy)_2dhp^{2+}$ complex.

For the reduced forms, the absorption spectrum of $Ru(bpy)_2dpp^+$ is almost identical to that of $Ru(dpp)_3^+$ (compare Figures 3 and 5). This provides strong support for the localization of an electron on the dpp ligand in preference to the bpy ligand, as might be expected from the relative values of their reduction potentials.[28] Any small differences in these two spectra may therefore be attributable to slight differences in the absorption of the coordinated ligands, bpy and dpp, in this region. In DMF, the absorption spectrum of this species is not so intense above 500 nm.[16] In the excited state, $Ru(bpy)_2dpp^{2+*}$ has a spectrum characteristic of a MLCT state with a ligand-localized electron (see Figure 5); i.e., there are bands centered around 360 and 450 nm attributable to π–π^* transitions of the ligand anion radical (π_6–π_7 and π_7–π_{11}, respectively). The spectrum is very similar to that recorded in ethanolic solution by Berger.[16] Although the spectrum cannot be used to decide whether the electron is localized on bpy or dpp, the spectrum of the reduced form clearly indicates a preference for localization on dpp.

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The spectrum of $Ru(bpy)_2dhp^+$ is quite different from that of $Ru(dhp)_3^+$ (compare Figures 1 and 6) in that it is about a third less intense and seems to have one or possibly two bands instead of the three bands characteristic of $Ru(dhp)_3^+$. When compared to the $Ru(bpy)_3^+$ spectrum,[7] the spectrum is similar in shape and intensity in the 400–500-nm region, but at longer wavelengths up to about 600 nm, $Ru(bpy)_3^+$ has a significantly stronger absorption than $Ru(bpy)_2dhp^+$.

The excited-state spectra of $Ru(dhp)_3^{2+}$ and $Ru(bpy)_2dhp^{2+}$ (see Figures 1 and 6) are very similar, particularly in the 400–600-nm region. The band at 360 nm characteristic of the MLCT state is also common to both spectra although the intensities differ by about 5000 $dm^3\ mol^{-1}\ cm^{-1}$. On the basis of the conclusion already made for $Ru(dhp)_3^{2+*}$, the data support the localization of an electron on the dhp ligand in the mixed complex, $Ru(bpy)_2dhp^{2+}$. Again, this would be consistent with the relative values of the reduction potentials of bpy and dhp.[28]

Binuclear Complexes. Although the difference extinction coefficients are relatively low in the region 300–470 nm for the excited states of the binuclear complexes (Figures 7 and 8), the values are sufficiently high between 500 and 600 nm to allow some confidence in using the corrected spectra in Figures 7 and 8 for interpretative purposes. Comparison of the MLCT excited-state absorption of $Ru(bpy)_2dpp(bpy)_2Ru^{4+}$ (Figure 8) with that measured by Berger in ethanolic solution[16] shows a clear difference at 550 nm, where there is little or no absorption in the latter work. In that study, Berger relied on the use of large laser pulses to completely convert the ground state. Although, this may give rise to the possibility of biphotonic processes, there is no need to make assumptions about the quantum yield of the excited states of the binuclear complexes as is the case here for the comparative technique using the $Ru(bpy)_3^{2+*}$ absorption as a standard. It is interesting to note that, in studies of the transient absorption spectra of binuclear ruthenium(II) complexes bridged by 2,2-bis(2-pyridyl)bibenzimidazole and similar ligands, it was not possible to convert more than 50% of the ground state using high-energy laser pulses.[14] This was attributed to the annihilation of excited states when there is sufficient energy to excite both ruthenium(II) ions. This may account for the differences in the MLCT excited-state spectra of $Ru(bpy)_2dpp(bpy)_2Ru^{4+}$ recorded in this and Berger's study. The alternative explanation is that the quantum yields of the MLCT excited states of binuclear complexes are much less than unity. However, from our complete conversion experiments, a value close to unity (0.9 ± 0.1) was obtained for $Ru(bpy)_2dhp(bpy)_2Ru^{4+}$ in acetonitrile. The spectra of the two binuclear complexes in their ground states are substantially different from those of the corresponding mononuclear complexes, $Ru(bpy)_2dhp^{2+}$ and $Ru(bpy)_2dpp^{2+}$, in that there are maxima at 420 and 530 nm instead of a band centered at 460 nm. These have been assigned, for the dpp complex, to Ru(II)–bpy MLCT and Ru(II)–dpp MLCT transitions, respectively, and similar assignments are made here for the dhp complex.

In the pulse radiolysis experiments, only one electron can be added to the binuclear complexes and hence only one electron localized on the ligands. The spectra of the one-electron-reduced forms of the two binuclear complexes shown in Figures 7 and 8 are quite similar, showing broad absorptions in the region 440–500 nm with extinction coefficients of about 20 000–24 000 $dm^3\ mol^{-1}\ cm^{-1}$. The magnitude of the extinction coefficients is approximately double that of the respective reduced monomeric complexes, reflecting probably the higher extinction coefficients of the binuclear ground states. The spectra are quite similar, qualitatively, to the spectra of $Ru(bpy)_2dpp^+$ and $Ru(bpy)_2dhp^+$, and it may be tentatively assumed that the single electron from the reduction process becomes localized on dpp and dhp, respectively, in these complexes, again consistent with the relative reduction potentials of the ligands.[28] Further support for this comes from cyclic voltammetry experiments on the dpp complex in DMF solutions, where the first reduction was proposed to occur on the dpp ligand.[16]

Excited-State Lifetimes. The lifetimes of the various mono- and binuclear complexes are listed in Table 2. For a given solvent, the lifetimes of $Ru(dhp)_3^{2+*}$, $Ru(dpp)_3^{2+*}$, and $Ru(dpq)_3^{2+*}$ are all shorter than those of $Ru(bpy)_3^{2+*}$ in the same solvent.[1] The lifetimes are such that the order is $Ru(dpq)_3^{2+*} < Ru(dpp)_3^{2+*} < Ru(dhp)_3^{2+*}$. For the mixed complexes, $Ru(bpy)_2dpp^{2+}$ and $Ru(bpy)_2dhp^{2+}$, the lifetimes of the excited states in all solvents are again much shorter than those of $Ru(bpy)_3^{2+}$ in the same solvents. In the case of the two binuclear complexes, within experimental error, the lifetimes are identical in all three solvents and are significantly shorter, by a factor of about 3, than the lifetimes of the related mixed-ligand mononuclear complexes, $Ru(bpy)_2dpp^{2+*}$ and $Ru(bpy)_2dhp^{2+*}$.

The lifetimes of the excited states of ruthenium(II) polypyridyl complexes are determined by the populations of both MLCT and metal-centered (MC or d–d) states. There are three[30] (or perhaps four[31]) MLCT states, and it is from these states that emission takes place. At 200 K and higher temperatures, each of these states is populated and contributes to the excited-state decay. As the temperature is increased above 200 K, population of d–d states begins. There are thus two channels from which radiative and nonradiative decay processes can occur. A well-established equation which has been useful in predicting the overall decay rate over a wide range of temperature is[32]

$$1/\tau(T) = k + k^\circ \exp[-(\Delta E/RT)]$$

where τ is the overall emission lifetime arising from the excited state, k represents both the radiative and nonradiative decay rates from the MLCT states (i.e., $k = k_r + k_{nr}$), and k° is a preexponential factor which may represent a situation either where MLCT and d–d states are in equilibrium (there being a relatively slow decay rate from the d–d state itself (10^9–$10^{10}\ s^{-1}$)) or where the rate of MLCT → d–d surface crossing is 10^{12}–$10^{14}\ s^{-1}$. Although there are examples of both, the latter is more usual, where typical ΔE values of the order 3000–4000 cm^{-1} are found.[32]

Clearly, factors which can change the relative populations of these two states may have a large influence on the overall emission decay rate. Caspar and Meyer[32] discussed the effect of solvent on $Ru(bpy)_3^{2+*}$ emission lifetimes by considering the MLCT and d–d states separately. For the MLCT state, they showed k_r to be relatively insensitive to solvent, as expected, since k_r is proportional to the cube of the emission energy for a spontaneous emission. The emission energies for $Ru(bpy)_3^{2+*}$ in a wide range of solvents were found to vary by about 3% only. In considering the effect of solvent on the nonradiative decay on the MLCT states, the same authors demonstrated that the decay rate obeyed the energy gap law and thus correlated well with the variation in emission energy as the solvent was varied. Despite this, however, the authors noted that hydroxylic solvents did not fit this correlation. For example, higher values than predicted were found in water. Other factors, such as increased electron delocalization in the acceptor ligand, may also affect the excited-state lifetime.[33]

The transition between the MLCT and d–d states was treated by Caspar and Meyer as a thermally-activated electron-transfer process from which there are clear solvent dependencies arising through both intramolecular and solvent classical vibrational trapping energies, which in turn are related to the optical and static dielectric constants of the medium. Although these authors did not expand on this treatment, they demonstrated from

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experiment that $k°$ varied from 2.6×10^{12} to 5.8×10^{13} s^{-1} in changing the solvent from *n*-butanenitrile to acetonitrile. Furthermore, there was a linear correlation between $k°$ and ΔE.

Another aspect of the effect of solvent is that photosubstitution has been shown to occur via the d–d state[32] and is very solvent dependent. Here, the solvent effect involves dissociation of one of the bipyridyl ligands originating from the decay of the d–d state. It is not clear whether such processes have any direct effect on the nonradiative decay of the d–d states.

It is difficult to relate the lifetime data obtained here in a meaningful way to parameters such as the emission energy, redox data, etc. This is particularly so when the hydroxylic solvents appear to behave differently from nonhydroxylic solvents. Nevertheless, there are some relationships which may be valid. The emission energy of $Ru(dpq)_3^{2+*}$ in acetonitrile (14.0×10^3 cm^{-1})[28] is much lower than those of $Ru(dhp)_3^{2+*}$ (15.4×10^3 cm^{-1})[28] and $Ru(dpq)_3^{2+*}$ (14.0×10^3 cm^{-1}).[28] Other factors being equal, this would indicate faster radiative and nonradiative decay from the MLCT states. Furthermore, the reduction potential (in DMF) of dpq (−1.56 V) is less negative than those measured for dhp (−1.76 V) and dpp (−1.9 V).[28] This may destabilize (relative to dpp and dhp complexes) the $Ru(dpq)_3^{2+}$ MLCT states with respect to the d–d state and hence facilitate greater population of the faster decaying d–d states. The observation that the lifetime of $Ru(dpq)_3^{2+*}$ is 3–4 times shorter than those observed for the dhp and dpp complexes provides some support for this interpretation.

The lifetimes of the excited states of the binuclear complexes were found to be shorter than those of the corresponding mononuclear (mixed or unmixed ligand) complexes. Similar observations were made by Berger,[16] but no explanation was offered. The interpretation of the very short lifetimes is likely to involve metal–metal interaction in the binuclear complexes. If in the excited state of binuclear complexes significant metal–metal interaction were to occur, the π^*-acceptor orbital may be distorted toward the second metal center, which may lead to an efficient nonradiative deactivation. Another possible explanation may involve the second $Ru(bpy)_2^{2+}$ moiety acting like a weak electron-withdrawing substituent, which may behave similarly to electron-withdrawing substituents in tris(polypyridine)ruthenium(II) complexes. For example, when a NO_2 group is substituted onto the 5-position of ruthenium tris(phenanthroline), the emission lifetime is reduced from 920 ± 100 ns to ≤5 ns.[34]

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