Inorg. Chem. **1996,** *35,* 2127−2131 **2127**

Coexistence of Ligand Localized and MLCT Excited States in a 2-(2′-Pyridyl)benzo[*g*]quinoline Complex of Ruthenium(II)

Emmanuelle Taffarel,[‡] Sarah Chirayil,[‡] Won Y. Kim,[†] Randolph P. Thummel,*[,‡] and Russell H. Schmehl*[,†]

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, and Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received November 10, 1994[⊗]

The photophysical behavior of complexes of the type $[(bpy)_2Ru(L)](PF_6)_2$, where L is a 2-(2′-pyridyl)quinoline or 2-(2′-pyridyl)benzo[*g*]quinoline derivative, was investigated in acetonitrile solutions and ethanol-methanol glasses. The luminescence from each complex originates from a metal-to-ligand charge transfer excited state and the energy of the emission maxima correlate with other reported quinoline complexes of Ru(II). The 2-(2′-pyridyl)benzo[*g*]quinoline complex has a unique transient absorption spectrum with a decay rate constant approximately 30 times less than the luminescence decay rate constant, indicating the existence of two nonequilibrated excited states in the complex. Comparison with other related complexes suggests the long-lived transient absorption may be due to a ligand localized ($\pi \rightarrow \pi^*$) excited state. The pyridylquinoline complex exhibits behavior characteristic of a single MLCT excited state.

Introduction

The photophysical behavior of transition metal complexes contains numerous examples of complexes which exhibit luminescence from metal-to-ligand charge transfer (MLCT) excited states[1−3] and complexes which also exhibit emission from excited states that can formally be described as ligand localized states.[4] Far fewer examples exist of complexes having two coexisting spectroscopically observable excited states.[3c,5−10] Some metalloporphyrins exhibit phosphorescence and delayed fluorescence resulting from intersystem crossing from the triplet back to the higher energy singlet excited state.[32] A variety of Rhenium(I) diimine complexes show evidence of luminescence from both ^{3}MLCT and intraligand (^{3}IL) excited states.[6−8] In addition, examples exist of dual luminescence from ^{3}IL and metal centered (d−d) states as well as luminescence from two different ^{3}IL states in mixed ligand complexes.[9,10] More subtle are complexes which luminesce from one state, but populate a second state which is detectable only via techniques other than luminescence measurements. Recently we have prepared several Ruthenium(II) diimine complexes which have unique transient absorption spectra with decay rates differing substantially from those of the observed luminescence.[8] The free energy dependence for luminescence quenching with a series of triplet energy quenchers differs from that for quenching of the transient absorbance, and the implication is that the transient absorbance is associated with a ^{3}IL state. In this work the photophysical behavior of Ru(II) complexes of the ligands shown below is described. For complexes of the type $[(bpy)_2Ru(L)]$, the complex containing **dmpq** exhibits a photophysical behavior similar to that of other pyridylquinoline complexes previously reported. The complex having **dmpbq** shows clear evidence for the coexistence of different nonemissive and luminescent states.

Experimental Section

The syntheses of the ligands, 3,3′-dimethylene-2-(2′-pyridyl)quinoline (dmpq)[11a] and 3,3′-dimethylene-2-(2′-pyridyl)benzo[*g*]quinoline (dmpbq)[11b] have been reported elsewhere. The complexes $[(bpy)_2Ru(dmpq)](PF_6)_2$ and $[(bpy)_3Ru]Cl_2$ were available from previous work.[8,11c] Acetonitrile used in all spectroscopic experiments was distilled from CaH_2 prior to use. NMR spectra were obtained using a General Electric QE-300 NMR spectrometer. Uv−vis spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer.

Complex Syntheses. $[Ru(dmpbq)(bpy)_2](PF_6)_2$. In EtOH−$H_2O$ (1:1, 10 mL) was dissolved dmpbq (28.2 mg, 0.1 mmol) and $[Ru(bpy)_2$-

---

[†] Tulane University.

[‡] University of Houston.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *82*, 85 and references therein.

(2) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

(3) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Johnson, S. R.; Westmoreland, T. D.; Caspar, J. V.; Barqawi, K. R.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3195. (c) Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389.

(4) (a) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647. (b) Hillis, J. E.; DeArmond, M. K. *J. Lumin.* **1971**, *4*, 273. (c) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Tucci, A.; Balzani, V. *Chem. Phys. Lett.* **1982**, *89*, 101. (d) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Chem. Phys. Lett.* **1984**, *104*, 100.

(5) (a) Chassot, L.; von Zelewsky, A.; Sandirini, D.; Maestri, M. Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6085. (b) Zuleta, J. A.; Bevilacqua, J. M.; Rehm, J. M.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 1332.

(6) (a) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (b) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888. (c) Wrighton, M. S.; Morse, D. L.; Pdungsap, L. *J. Am. Chem. Soc.* **1975**, *97*, 2073.

(7) (a) Zipp, A. P.; Sacksteder, L.; Streich, J.; Cook, A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1993**, *32*, 5629. (b) Sacksteder, L.; Lee, M.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1993**, *115*, 8230.

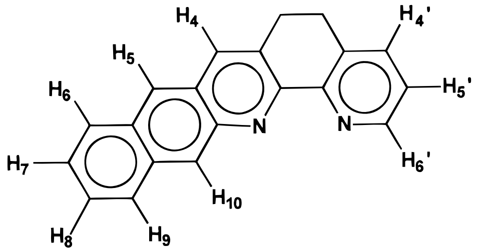
(8) (a) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.*, submitted for publication. (b) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389.

(9) (a) Segers, D. P.; DeArmond, M. K.; Grutsch, P. A.; Kutal, C. *Inorg. Chem.* **1984**, *23*, 2874. (b) Merrill, J. T.; DeArmond, M. K. *J. Am. Chem. Soc.* **1979**, *101I*, 2045. (c) Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225. (d) Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 4895.

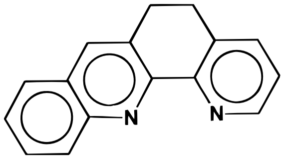
(10) (a) Wilde, A. P.; King, K. A.; Watts, R. J. *J. Phys. Chem.* **1991**, *95*, 629. (b) King, K. A.; Watts, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 1589. (c) Watts, R. J.; Efrima, S.; Metiu, H. *J. Am. Chem. Soc.* **1979**, *110*, 2742. (d) Watts, R. J.; Van Houten, J. *J. Am. Chem. Soc.* **1978**, *100*, 1718.

(11) (a) Thummel, R. P.; Decloitre, Y.; Lefoulon, F. *J. Heterocycl. Chem.* **1986**, *23*, 689. (b) Taffarel, E.; Chirayil, S.; Thummel, R. P. *J. Org. Chem.* **1994**, *59*, 823. (c) Thummel, R. P.; Decloitre, T. *Inorg. Chim. Acta* **1987**, *128*, 245.

0020-1669/96/1335-2127$12.00/0



dmpbq



dmpq

$Cl_2(H_2O)_2]$[12] (43.1 mg, 0.085 mmol). The solution was refluxed for 17 h and then cooled to room temperature. NH_4PF_6 (56 mg, 0.35 mmol) was added, and the solution was stirred at room temperature for 3 h. The red precipitate was vacuum filtered to afford 40 mg (48%) of a solid which was recrystallized from toluene/CH_3CN (1:1). The ^1H NMR of the complex exhibited the correct aliphatic:aromatic proton ratio of 26:4 and complete characterization was accomplished via the analogous bpy-d_8 complex.

[Ru(dmpbq)(bpy-d_8)$_2$](PF$_6$)$_2$. The procedure described above was followed using dmpbq (14.1 mg, 0.05 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$-(H$_2$O)$_2$][13] (23.5 mg, 0.0425 mmol) to provide 28 mg (68%) of a red crystals: ^1H NMR (300 MHz, CD_3CN) δ 8.52 (s, 1H, H_5), 8.41 (s, 1H, H_4), 8.03 (d, 1H, $J = 8.5$ Hz, H_6), 7.92 (d, 1H, $J = 7.5$ Hz, $H_{4'}$), 7.85 (s, 1H, H_{10}), 7.54 (dt, 1H, H_7), 7.53 (d, 1H, $J = 6.5$ Hz, $H_{6'}$), 7.43 (dt, 1H, H_8), 7.35 (dd, 1H, $H_{5'}$), 7.11 (d, 1H, $J = 8.5$ Hz, H_9). The 2D COSY spectrum of this complex is available as supplementary material.

Luminescence Measurements. Room temperature luminescence spectra and quantum yields were obtained in freeze pump thaw degassed acetonitrile solutions of the complexes. Spectra were obtained using a SPEX Fluorolog spectrofluorimeter equipped with a 450 W Xe arc lamp, thermostated cell holder, single grating monochromators with fixed slits, and a liquid N_2 cooled CCD detector. Spectra were not corrected for detector response. Quantum yields were measured relative to $[Ru(bpy)_3]Cl_2$ in H_2O.[14] Luminescence spectra at 77 K were obtained using the above equipment and 4:1 ethanol:methanol glasses containing the complexes.

Room temperature luminescence lifetimes were obtained by time correlated single photon counting using a home built instrument. The excitation source was an IBH System 5000 coaxial flashlamp filled with H_2; the excitation light was filtered through a Schott UG-1 bandpass filter and focused onto the sample in a thermostated cell. Luminescence from the sample was focused onto a Hammamatsu R928 PMT following filtering through Andover Co. narrow bandpass filters (± 10 nm). Electronics for signal discrimination and time to amplitude conversion were obtained from Tennelec Co. and included a Model TC 454 quad constant fraction discriminator and a Model TC 863 TAC/SCA. The output of the TAC was accumulated by a Viking Instruments/Norland Model 5000 MCA. Luminescence decay analysis was performed using a Marquardt algorithm for single and double exponential decays.[15] Luminescence decays at 77 K were measured following N_2 laser excitation using equipment described elsewhere. Transient absorption spectra were obtained with a nanosecond flash photolysis setup previously described.[16]

Results and Discussion

Complex Syntheses. The complex [Ru(dmpq)(bpy)$_2$](PF$_6$)$_2$ has been reported previously[11c] and the complex [Ru(dmpbq)-(bpy)$_2$](PF6)$_2$ was prepared in the usual manner. To facilitate identification of the latter complex, we also prepared [Ru-(dmpbq)(bpy-d_8)$_2$](PF$_6$)$_2$, which simplified the aromatic region of the ^1H NMR sufficiently to allow complete assignment of a 2D COSY spectrum (Supporting Information).

Redox and Spectroscopic Behavior. The complexes of dmpq and dmpbq represent additions to the large number of complexes having the formula $[(bpy)_2Ru(L)]^{2+}$, where L is a bidentate ligand.[1−3] The extensive work of several research groups has resulted in various general correlations of redox and spectroscopic properties of this class of complexes when L represents a series of structurally related ligands. Absorption and luminescence maxima of MLCT transitions are linearly related to the difference between the potentials for one electron oxidation and reduction of the complexes, $\Delta E°$.[17−19] In addition, rate constants for nonradiative relaxation from the MLCT state in series of the complexes have been shown to follow "golden rule" behavior wherein a linear relationship exists between ln k_{nr}, where k_{nr} is the nonradiative decay rate constant of the complex and E_{em} is the emission energy.[3,24] These observations are consistent with high efficiency population of a single excited state which is charge transfer in character. The complexes in the series reported in this work contain diimine ligands with quinoline or benzo[*g*]quinoline functionalities. The photophysical behavior of the quinoline derivative is similar to that of related complexes reported earlier, however, the benzo[*g*]-quinoline complex exhibits unique differences. Results for the two complexes are given below; correlation with complexes previously reported is also made.

Redox Behavior. Table 1 gives potentials for the one electron oxidation and one electron reduction of each complex, labeled *E*(III/II) and *E*(II/I), respectively. The potentials were obtained by cyclic voltammetry in acetonitrile solutions. Both *E*(III/II) and *E*(II/I) appear to be both chemically ($i_{p,a}/i_{p,c} = 1$) and electrochemically ($\Delta E_p \sim 60$ mV) reversible. In each case the voltammetric waves correspond to one electron processes. Included in Table 1 also are potentials for other quinoline or

---

[12] Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

[13] Thummel, R. P.; Chirayil, S. *Inorg. Chem.* **1989**, *28*, 812.

[14] Kawanishi, Y.; Kitamura, N.; Kim, Y.; Tazuke, S. *Riken Q.* **1984**, *78*, 212.

[15] Bevington, P. R. Data Reduction and Error Analysis for the Physical Sciences; McGraw-Hill: New York, 1969; pp 235−245.

[16] Shaw, J. R.; Webb, R. T.; Schmehl, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1117.

[17] (a) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444. (b) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D.; *Inorg. Chem.* **1983**, *22*, 1617.

[18] Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849. Wallace, L.; Rillema, D. P. *Inorg.Chem.* **1993**, *32*, 3836.

[19] Juris, A.; Belser, P.; Barigelletti, G.; von Zelewsky, B; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256.

[20] See *The Merck Index*, 10th ed.; Merck & Co.; Rahway, NJ, 1983; pp 5065, 7997.

[21] Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 3032.

[22] Ohsawa, Y.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 229.

[23] (a) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841. (b) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177. (c) Bolletta, F.; Juris, A.; Maestri, M.; Sandrini, D. *Inorg. Chim. Acta* **1980**, *44*, L175.

[24] (a) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (b) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. (c) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630−632.

[25] Lacish, U.; Infelta, P. P.; Gratzel, M. *Chem. Phys. Lett.* **1979**, *62*, 317.

[26] Braterman, P.; Harriman, A; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801.

Table 1. Redox Potentials, Absorption Maxima, and Luminescence Maxima in Acetonitrile Solutions at Room Temperature for $[(bpy)_2Ru(L)](PF_6)_2$ Complexes[a]

ligand L[b]	E(III/II), V	E(II/I), V	ΔE, V	λ_{max}, nm (eV)	E_{em}, nm (eV)	ref
bpy	1.26	−1.34	2.6	452 (2.74)	614 (2.02)	1
dmpq	1.31	−1.11	2.42	480 (2.58)	680 (1.82)	this work
dmpbq	1.32	−0.95	2.27	512 (2.42)	780 (1.60)	this work
biq	1.33	−0.91	2.24	526 (2.36)	742 (1.67)	25
DMCH	1.25	−1.00	2.25	528 (2.34)	736 (1.68)	26
pyq	1.27	−1.13	2.40	478 (2.59)	700 (1.77)	27
ibiq	1.22	−1.38	2.60	450 (2.75)	610 (2.03)	28

[a] Redox potentials vs SSCE; supporting electrolyte is tetraethylammonium perchlorate. [b] Key: biq = 2,2′-biquinoline; DMCH = 5,6-dihydro-4,7-dimethyldibenzo[3,2-*b*:2′,3′-*j*]-1,10-phenanthroline; pyq = 2-(2-pyridyl)quinoline; ibiq = 2,2′-isobiquinoline.

isoquinoline derivatives previously reported.[27−30] The one electron oxidation is metal localized for all the complexes (eq 1). As can be seen from the table, variations in L result in

$$[(bpy)_2Ru^{III}(L)]^{3+} + e^- \rightleftharpoons [(bpy)_2Ru^{II}(L)]^{2+} \qquad (1)$$

only small changes in E(III/II). It is interesting to note that the most important factor influencing E(III/II) in this series is the position of the benzo ring in the quinoline or biquinoline. Since E(III/II) is a metal-centered process, the potential will most directly relate to the relative electron density on the heteroatoms composing the coordination sphere; for diimine ligands this is directly related to the pK_a of the nitrogen base. The pK_a values for the hydrochloride salts of quinoline and isoquinoline are 4.5 and 5.4 respectively,[20] consistent with the relative difference in E(III/II) observed between the **biq** and **ibiq** complexes. The relatively low Ru(III/II) potential of the DMCH complex, a quinoline derivative, results from the addition of two methyl groups to the ligand.

The E(II/I) potential represents reduction of the most easily reduced diimine ligand which is the unique ligand (eq 2) in

$$[(bpy)_2Ru(L)]^{2+} + e^- \rightleftharpoons [(bpy)_2Ru(L^-)]^{+} \qquad (2)$$

each case except for 2,2′-bipyridyl and isobiquinoline (ibiq) derivatives, for which the reduction may be either bpy localized or rapidly equilibrating by intramolecular electron hopping between ligands.[21] Previous ESR[21] and resonance raman spectral studies[31] indicate that the electron is preferentially localized on the most easily reduced ligand unless reduction potentials of the ligands vary by less than approximately 100 mV. One electron reduction of $[(bpy)_3Ru]^{2+}$ occurs at −1.35 V vs SCE in acetonitrile[22] while reduction of most of the quinoline or biquinoline complexes occurs at potentials 200−300 mV positive relative to the bpy-localized reduction.

Absorption and Luminescence Properties. Absorption maxima for the lowest energy metal-to-ligand charge transfer (MLCT) transition of each complex are given in Table 1. The absorption involves either Ru(dπ) → bpy(π*) or Ru(dπ) → L(π*) transitions. In general, the lowest energy MLCT transition for a series of complexes having very similar coordination spheres (i.e. all imine type nitrogen heterocycles) will involve the ligand having the lowest one electron reduction potential. For the complexes listed in Table 1, the lowest energy MLCT transition is Ru(dπ) → L(π*) for all of the ligands except bpy and ibiq. The difference in ligand π* levels between bpy and ibiq is small enough that MLCT transitions to particular ligands are not resolved. As stated earlier, for series of complexes having charge transfer transitions the relative absorption maxima for the lowest energy MLCT transition should be linearly related to the difference between electrochemical potentials for one electron oxidation and reduction.[17−19] Figure 1A shows the correlation obtained for this series of complexes. Values for the dmpq and dmpbq complexes, shown as triangles in the figure, follow the trend of the series.

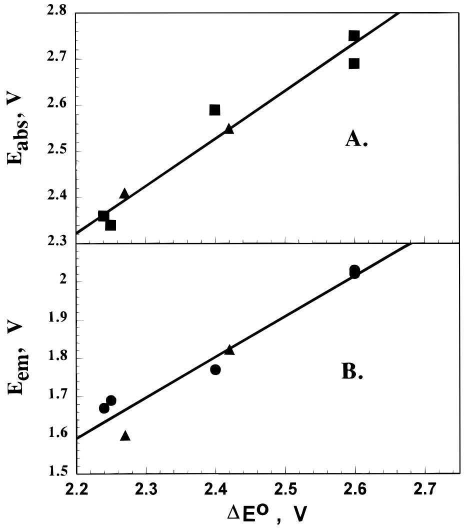


Figure 1. Energies of absorption maxima (A) and luminescence maxima (B) for quinoline containing complexes as a function of $\Delta E°$, the difference in one electron oxidation and reduction potentials for the complexes in room temperature acetonitrile solutions. Filled triangles correspond to dmpq and dmpbq complexes.

The luminescence maxima for the series of complexes in room temperature acetonitrile are also given in Table 1. Luminescence is typically only observed from the lowest energy ^{3}MLCT state in room temperature solutions of metal diimine complexes. The ^{3}MLCT state results from intersystem crossing from the ^{1}MLCT state(s) and has been shown to form in high yield for several ruthenium(II) diimine complexes.[23] Exceptions exist for complexes where the lowest energy state is ligand localized, yielding structured phosphorescence from the ^{3}IL state; this is frequently observed for Rh(III), Ir(III), and Pt(II) complexes of phenanthroline.[4−10,23] As with MLCT absorption, luminescence from MLCT states for a series of complexes is linearly related to $\Delta E°$. The results for this series are shown in Figure 1B. With the exception of the dmpbq complex, a reasonable linear correlation exists with a slope of 1.03. The fact that the dmpbq complex does not fit in the series may suggest that luminescence from this complex is from a state other than a purely MLCT state (*vide infra).*

More detailed information on the complexes examined in this work is given in Table 2 including the luminescence lifetimes for the dmpq and dmpbq complexes at room temperature, luminescence quantum yields in room temperature acetonitrile, calculated radiative decay rate constants, and emission maxima in 4:1 ethanol:methanol glasses at 77 K. The results indicate

---

(27) (a) Juris, A; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Isr. J. Chem.* **1982**, *22*, 87. (b) Klassen, D. M. *Chem. Phys. Lett.* **1982**, *93*, 383.

(28) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 2175.

(29) Gaines, G. L. *Inorg. Chem.* **1980**, *19*, 1710.

(30) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202.

(31) (a) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492. (b) Yabe, T.; Orman, L. K.; Anderson, D. R.; Yu, S.-C.; Xu, X.; Hopkins, J. B. *J. Phys. Chem.* **1990**, *94*, 7128. (c) Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613.

(32) (a) Lukomsky, I.; Gottfried, V.; Kimel, S. *J. Fluoresc.* **1994**, *4*, 49. (b) Feitelson, J.; Barboy, N. *J. Phys. Chem.* **1986**, *90*, 271.

Table 2. Luminescence Properties of $[(bpy)_2Ru(L)]^{2+}$ Complexes in Room Temperature CH_3CN and 4:1 Ethanol:Methanol Glasses at 77 K and Transient Absorption Lifetimes in Room Temperature CH_3CN

	298 K				77 K
ligand	τ_{em}, ns[a]	ϕ_{em}	$k_r \times 10^4$, s^{-1}	τ_{abs}, ns[b]	E_{em}, nm (eV)
dmpq	660	0.01	2.1	720	650 (1.90)
dmbpq	35	0.0006	1.7	960	770 (1.61)
bpy[c]	860	0.086	10.0	800	580 (2.13)

[a] Lifetimes ±10%. [b] Lifetimes ±15%. [c] Reference 12.

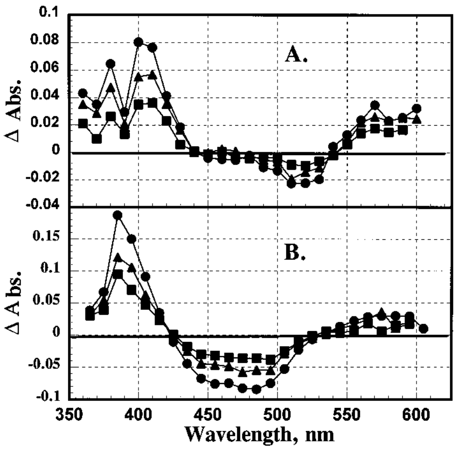


Figure 2. Transient absorption spectra of (A) $[(bpy)_2Ru(dmpbq)](PF_6)_2$ at 0.25 (●), 0.5 (▲), and 1 (■) μs after excitation and (B) $[(bpy)_2Ru(dmpq)](PF_6)_2$ at 0.25 (●), 0.5 (▲), and 0.75 (■) μs after excitation in acetonitrile solutions at room temperature.

that the dmpbq complex exhibits much weaker luminescence and has a much shorter lifetime than the dmpq complex in solutions at room temperature. The shorter lifetime is expected based upon consideration of the energy gap law for nonradiative relaxation.[3,24] The radiative decay rate constants were calculated simply from the ratio of the luminescence quantum yield and lifetime ($k_r = \phi_{em}/\tau_{em}$). Assuming luminescence is from a ^{3}MLCT state which is populated by intersystem crossing from a ^{1}MLCT state, the observed radiative decay rate constant represents the product of the intersystem crossing efficiency and the radiative decay rate costant, $\eta_{isc}k_r$. For $[Ru(bpy)_3]^{2+}$ and several other Ru(II) complexes having three diimine ligands, the value of η_{isc} has been determined to be unity.[23] Results of numerous previous studies yield observed k_r values for Ru(II) diimine complexes between 5 and 10 × 10^4 s^{-1} and the values for the dmpq and dmpbq complexes are somewhat low. The simple implication is that η_{isc} is less than unity which indicates that either the ^{1}MLCT state relaxes back to the ground state exceedingly rapidly or another excited state is formed by an independent intersystem crossing process. If intersystem crossing does occur from the ^{1}MLCT state to another excited state, it is possible that excitation into ligand-localized states will lead to relaxation into states other than the ^{3}MLCT state. It should be noted that corrected excitation spectra for ^{3}MLCT emission of both complexes are very similar to the absorption spectra. Excitation into ligand localized absorption bands does result in population of the emitting MLCT excited state. Even at 77 K luminescence is exclusively from the ^{3}MLCT state, in contrast to Re(I) complexes which exhibit structured luminescence from a ligand localized state in frozen solutions.[4-10]

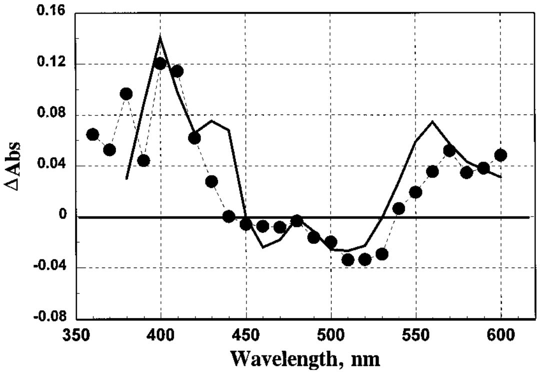


Figure 3. Transient absorption spectrum of $[(bpy)_2Ru(dmpbq)](PF_6)_2$ (--●--) and spectrum calculated by subtracting ground state absorption of $[(bpy)_2Ru(dmpbq)](PF_6)_2$ from the transient absorption spectrum dmpbq (—).

Transient Absorption Spectra. Excited state absorption spectra of dmpq and dmpbq complexes are shown in Figure 2. In all cases excitation was with the 308 nm emission of a $XeCl_x$ excimer laser; typical intensities were <10 mJ per pulse, and intensity dependence studies indicate the transients observed were formed via monophotonic excitation in each case. The dmpq complex has a transient spectrum characteristic of complexes having ^{3}MLCT excited states. The spectrum includes a strong absorption betwen 350 and 400 nm, characteristic of the dmpq anion radical ($\pi \rightarrow \pi^*$), and bleaching in the 425–500 nm region reflects loss of the ground state MLCT absorption. The additional weak absorption between 550 and 600 nm has been assigned for $[(bpy)_3Ru]^{2+}$ as a $\pi \rightarrow \pi^*$ transition of the bpy anion of the excited state.[25,26] The decay of the transient absorbance is single exponential and the decay rate constant obtained is within experimental error of the luminescence lifetime (Table 2).

Transient absorption of the dmpbq complex shows a sharp departure from the luminescence behavior. A transient is observed with a lifetime of nearly 1 μs, in contrast to the 35 ns lifetime observed for the luminescence. The vast difference in decay rate constants clearly indicates that two different non-equilibrated excited states exist. The observed transient spectrum differs in relatively subtle ways from the spectrum of the dmpq complex. The general trend of a strong absorption in the blue, bleaching of the ground state absorption and a weaker absorption in the green and red is observed for this complex. However, the relative absorptivity of the green/red absorption is half that of the blue absorption while for the dmpq complex the green/red absorption has an absorptivity which is at most 15% that of the blue absorbance. While it is possible that a MLCT excited state is responsible for the transient absorbance, it is also conceivable that the excited species is a ligand localized triplet, ^{3}IL, state. Alternatively, the excited state may form an excited state complex (exciplex) with the solvent. Direct excitation of a degassed solution of the dmpbq ligand yields a transient having absorption maxima at 400 and 440 nm with broad absorption continuing into the green; the green absorption has slightly less than half the molar absorptivity of that of the 400 nm maximum. Subtraction of the ground state absorption spectrum from the transient spectrum of dmpbq yields the spectrum shown in Figure 3. The solid line represents the calculated spectrum and the solid points are those obtained for $[(bpy)_2Ru(dmpbq)]^{2+}$. While the correspondence of the two spectra is not exact, the spectral trends suggest the ^{3}IL state assignment is not unreasonable.

An alternative explanation for the long-lived transient is exciplex formation with the solvent. Watts and co-workers have recently shown that exciplexes form between 8-quinolylphenylmethylsilane complexes of Ir(III) and σ donating and π

accepting solvents.[33] Vastly different lifetimes are observed between the luminescence decay and the decay of ground state bleaching and luminescence lifetimes are solvent dependent, varying by more than a factor of 5 between acetonitrile and butanol. In addition the transient spectrum evolves from that of the initial charge transfer state to a spectrum which shows only ground state bleaching. For $[(bpy)_2Ru(dmpbq)]^{2+}$ the lifetime varies only slightly between acetonitrile, ethanol and CH_2Cl_2 and the transient spectrum is invarient at times greater than 100 ns.[34] Thus, while exciplex formation cannot be excluded, the absence of a solvent dependence for the luminescence and transient absorbance decays and the similarity of the transient spectrum obtained with the spectrum generated from the ligand transient and the complex ground state absorption lead us to favor a ^{3}IL assignment for the long-lived transient absorbance.

The results for dmpq and dmpbq illustrate that examination of ground state absorption and luminescence is not necessarily adequate to fully describe the excited state photophysical behavior of the complexes. In this case it is apparent that the dmpbq complex has two nonequilibrated excited states and one of them is nonluminescent. Recent work from our own lab and the labs of Demas[7] and Rillema[18] have provided examples of complexes that exhibit luminescence from ^{3}IL states varying only slightly in energy from the luminescence of the noncoordinated ligands. In addition, comparison of the photophysical properties of aza derivatives of aromatic hydrocarbons with those of the hydrocarbons suggests that, for a given type of excited state, little change occurs upon inclusion of the heteroatom. The implication is that triplet energies of parent hydrocarbons can serve as reasonable approximations for the triplet energies of aza derivatives. For the complexes of dmpq and dmbpq the hydrocarbon analogs are naphthalene ($E_T = 2.6$ V) and anthracene ($E_T = 1.8$ V), respectively. Anthracene triplets are clearly lower in energy than the ^{1}MLCT state formed upon excitation while the naphthalene triplet is not energetically accessible from the ^{1}MLCT state. Thus there is significant evidence to suggest that intersystem crossing to a triplet ligand localized excited state (^{3}IL) can occur in complexes for which the ^{3}IL state is lower in energy than the ^{1}MLCT state. The dmpbq complex reported here may represent another complex exhibiting this behavior. We are presently examining other complexes having ligands which have extended delocalization which may result in low energy ligand-localized excited states.

Acknowledgment. R.H.S. wishes to acknowledge the support of the Office of Basic Energy Sciences of the U. S. Department of Energy under Grant DE-FG05-92ER14309. R.P.T. would like to thank the Robert A. Welch Foundation, the National Science Foundation (Grant CHE-9224686), and the Texas Higher Education Coordinating Board for financial support of this work.

Supporting Information Available: Figures showing the COSY spectrum of $[(bpy)_2Ru(dmpbq)](PF_6)_2$ and its structure and text discussing assignment of peaks (3 pages). Ordering information is given on any current masthead page.

IC9412973

---

(33) (a) Djurovich, P. I.; Watts, R. J. *J. Phys. Chem.* **1994**, *98*, 396. (b) Djurovich, P. I.; Cook, W.; Joshi, R.; Watts, R. J. *J. Phys. Chem.* **1994**, *98*, 398.

(34) The resolution of our present apparatus for transient absorption does not allow us to obtain reproducable data at times shorter than 100 ns.