

Effect of Delocalization and Rigidity in the Acceptor Ligand on MLCT Excited-State Decay

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In its most simple form, the energy gap law for excited-state nonradiative decay predicts a linear dependence of $\ln k_{nr}$ on the ground- to excited-state energy gap, where k_{nr} is the rate constant for nonradiative decay. At this level of approximation, the energy gap law has been successfully applied to nonradiative decay in a wide array of MLCT excited states of polypyridyl complexes of Re^I, Ru^{II}, and Os^{II}. This relationship also predicts a dependence of k_{nr} on the structural characteristics of the acceptor ligand. We report here a brief survey of the literature which suggests that such effects exist and have their origin in the extent of delocalization of the excited electron in the ligand π^* framework and on acceptor ligand rigidity.

Along with the $\pi-\pi^*$ excited states of porphyrins and metalloporphyrins, metal-to-ligand charge-transfer (MLCT) excited states of polypyridyl complexes have dominated the study of photoinduced electron and energy transfer in molecular assemblies.¹ Polypyridyl complexes of Ru(II), e.g. [Ru(bpy)₃]²⁺ (bpy is 2,2'-bipyridine), Os(II), and Re(I) have provided the majority of examples. The synthetic chemistry in this area (both at the metal and the ligands) has grown considerably, driven in part by the demands associated with preparing increasingly complex assemblies and model systems for refining theoretical concepts.² This chemistry has been used to prepare multicomponent molecular assemblies,³ derivatized soluble polymers,⁴ electropolymerized thin polymeric films,⁵ photoactive DNA cleavage agents,⁶ and photovoltaic cells based upon dye-sensitized, colloidal TiO₂.⁷

There is an extensive literature on MLCT excited states and much has been learned about electronic structure, coupled molecular vibrations, the role of low-lying excited states of different orbital origins, and medium effects.^{8–10} Much remains to be learned if ground- and excited-state properties (e.g. light absorption, excited-state lifetime) are to be optimized. An important molecular feature in these excited states is the acceptor ligand, the ultimate ligand of residence for the excited electron. In heteroleptic chelates, this is the ligand having the lowest π^* acceptor level.¹¹ For example, in [Ru(dmb)₂(bpy)]²⁺ (dmb is

4,4'-dimethyl-2,2'-bipyridine) the acceptor ligand is bpy (eq 1).



In some cases the acceptor ligand has been identified directly by transient resonance Raman spectroscopic measurements on

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- (1) (a) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part D, p 303. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991. (c) Gust, Moore, T. A. *Science* **1989**, *244*, 35. (d) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73. (e) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (f) Willner, I.; Willner, B. *Adv. Photochem.* **1995**, *20*, 217. (g) Scandola, F.; Bignozzi, C. A.; Indelli, M. T. *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kluwer Academic: Dordrecht, The Netherlands, 1993; pp 161–216. (h) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (i) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (j) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (k) Johnson, S. R.; Westmoreland, T. D.; Caspar, J. V.; Barqawi, K. R.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3195.

- (2) (a) Della Ciana, L.; Hamachi, I.; Meyer, T. J. *J. Org. Chem.* **1989**, *54*, 1731. (b) Katritzky, A. R.; Lang, H. Y.; Lan, X. F. *Tetrahedron* **1993**, *49*, 2829. (c) Geren, L.; Hahm, S.; Durham, B.; Millett, F. *Biochemistry* **1991**, *30*, 9450. (d) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7892. (e) Katz, N. E.; Mecklenburg, S. L.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 1282 and references therein. (f) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383. (g) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334. (h) Juris, A.; Baragelletti, S.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (i) Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanyon, C. B.; White, R. P. *Inorg. Chem.* **1989**, *28*, 1013. (j) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G. *Inorg. Chem.* **1988**, *27*, 3652. (k) von Zelewsky, A.; Gremaud, G. *Helv. Chim. Acta* **1988**, *71*, 1108. (l) Strouse, G. F.; Anderson, P. A.; Schoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004. (m) Hayoz, P.; von Zelewsky, A.; Stoeklievans, H. *J. Am. Chem. Soc.* **1993**, *115*, 5111. (n) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145–6157.
- (3) (a) Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 5295. (b) Mecklenburg, S. L.; Peek, B. M.; Schoonover, J. R.; McCafferty, D. G.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 5479. (c) Mecklenburg, S. L.; McCafferty, D. G.; Schoonover, J. R.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 2974. (d) Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, T. J. *Int. J. Peptide Protein Res.* **1991**, *38*, 114. (e) Mecklenburg, S. L.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 8540. (f) Peek, B. M.; Edwards, S. W.; Erickson, B. W.; Mecklenburg, S. L.; Meyer, T. J. In *Peptides: Chemistry, Structure, and Biology*; Smith, J. A., Rivier, J. E., Eds.; ESCOM: Leiden, The Netherlands, 1992. (g) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (h) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103. (i) Balzani, V.; Sabatini, N.; Scandola, F. *Chem. Rev.* **1987**, *86*, 319. (j) Petersen, J. D. *Coord. Chem. Rev.* **1985**, *64*, 261. (k) Krause, R. A. *Struct. Bonding (Berlin)* **1987**, *67*, 1. (l) Ferguson, J.; Herren, F.; Krausz, E. R.; Maeder, M.; Vrbrancich, J. *Coord. Chem. Rev.* **1985**, *64*, 21. (m) Creutz, C. P.; Chou, M.; Netzel, L.; Okumura, M.; Sutin, N. S. *J. Am. Chem. Soc.* **1980**, *102*, 1309. (n) Pankuch, B. J.; Lacky, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. (o) Lee, E. J.; Wrighton, M. S.; *J. Am. Chem. Soc.* **1991**, *113*, 8562.

the excited state.¹² The role of the acceptor ligand is the theme of this paper: specifically, how the manipulation of acceptor ligand structure can be used to control lifetime by exploiting

delocalization and rigidity and evidence from the literature that these are general effects.

Most polypyridyl complexes of Ru(II), Os(II), and Re(I) are sufficiently weak emitters that lifetimes are dominated by nonradiative decay. In this limit, the following relationships hold.

$$\tau^{-1} = k_r + k_{nr} \quad (2a)$$

$$\Phi_{em} = \tau k_r \quad (2b)$$

$$\tau^{-1} \sim k_{nr} \quad (2c)$$

In eqs 2, k_r and k_{nr} are the rate constants for radiative and nonradiative decay, Φ_{em} is the emission quantum yield, and τ is the lifetime. Nonradiative decay can include contributions from thermal population and decay through upper excited states. This is commonly the case for complexes of Ru(II), where low-lying dd states of orbital origin $(d\pi)^5(d\sigma^*)^1$ lie close in energy to the emitting MLCT state(s).^{8,12}

Nonradiative decay from MLCT states to the ground state is typically dominated by energy loss into a series of medium-frequency ring-stretching vibrations with energy spacings between 1000 and 1600 cm^{-1} .^{12,13} For purposes of analysis, these vibrations can be approximated as a single averaged mode of quantum spacing $\hbar\omega_M$ and electron–vibrational coupling constant S_M . S_M is related to the change in equilibrium displacement between the ground and excited state, ΔQ_e , and the reduced mass, M , by eq 3. In the limit that $E_0 \gg$

$$S_M = \frac{1}{2} \frac{M\omega}{\hbar} (\Delta Q_e)^2 \quad (3)$$

$S_M \hbar\omega_M$ and $\hbar\omega_M \gg k_B T$, k_{nr} varies with E_0 (the energy gap) according to the energy gap law, eqs 4.¹⁴ The first term

$$\ln k_{nr} = \ln(\beta_0) + \ln[F(\text{calc})] \quad (4a)$$

in this equation includes the vibrationally induced electronic coupling matrix element. Nonradiative decay is a transition between states whose electronic wave functions are solutions of the same Hamiltonian. To zero order, they can not mix. The states can be mixed, however, and the transition between states induced, by coupled vibrations of appropriate symmetry.

The second term in eq 4a contains the Boltzmann-weighted vibrational overlap factor, $F(\text{calc})$. The magnitude of k_{nr}

- (4) (a) Baxter, S. M.; Jones, W. E.; Danielson, E.; Worl, L. A.; Younathan, J.; Strouse, G. F.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47. (b) Younathan, J. N.; McClanahan, S. F.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 488. (c) Olmstead, J., III; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3297. (d) Younathan, J. N.; McClanahan, S. F.; Meyer, T. J. *Macromolecules* **1989**, *22*, 1048. (e) Margerum, L. D.; Meyer, T. J.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 2696. (f) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363. (g) Strouse, G. F.; Worl, L. A.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 9101. (h) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571.
- (5) (a) Abruna, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135. (b) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151. (c) Denisevich, P.; Abruna, C. R.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153. (d) Calvert, J. M.; Sullivan, B. P.; Meyer, T. J. In *Chemically Modified Surfaces In Catalysis and Electrocatalysis*; Miller, J., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1982; p 159. (e) Abruna, H. D.; Calvert, J. M.; Denisevich, P.; Ellis, C. D.; Meyer, T. J.; Murphy, W. R.; Murray, R. W.; Sullivan, B. P.; Walsh, J. L. In *Chemically Modified Surfaces In Catalysis and Electrocatalysis*; Miller, J., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1982; p 133. (f) Gould, S.; Gray, K.; Linton, R. W.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 5521.
- (6) (a) Neyhart, G. A.; Cheng, C.; Thorp, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1463. (b) Thorp, H. H.; Cheng, C.; Goll, J. G. *J. Am. Chem. Soc.* **1995**, *117*, 2970. (c) Thorp, H. H.; Cheng, C.; Johnson, D. H. *Inorg. Chem.* **1994**, *33*, 6388. (d) Smith, S. R.; Neyhart, G. A.; Kalsbeck, W. A. *New J. Chem.* **1994**, *18*, 397. (e) Grover, N.; Gupta, N.; Singh, P. *Inorg. Chem.* **1992**, *31*, 2014.
- (7) (a) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (b) O'Reagan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (c) Willig, F.; Eichberger, R. *Chem. Phys.* **1990**, *141*, 159. (d) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216. (e) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267. (f) Heimer, T. A.; Bignozzi, C. A.; Meyer, G. J. *J. Phys. Chem.* **1993**, *97*, 11987. (g) Bignozzi, C. A.; Meyer, G. J.; Argazzi, R. *Inorg. Chem.* **1994**, *33*, 5741.
- (8) (a) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803. (b) Porter, G. B.; Sparks, R. H. *J. Photochem.* **1980**, *13*, 123. (c) Rillema, D. P.; Blanton, C. B.; Shaver, R. J.; Jackman, D. C.; Boldaji, M.; Bundy, S.; Worl, L. A.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 1600. (d) Segers, D. P.; DeArmond, M. K. *J. Phys. Chem.* **1982**, *86*, 3768. (e) Gleria, M.; Minto, F.; Beggiano, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1978**, 285. (f) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (g) Barqawi, K. R.; Llobet, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7751. (h) Kirchoff, J. R.; McMillan, D. R.; Marnot, P. A.; Sauvage, J. *J. Am. Chem. Soc.* **1985**, *107*, 1138. (i) Lin, C. T.; Boettcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536. (j) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 3841.
- (9) (a) Chen, P.; Mecklenburg, S. L.; Meyer, T. J. *J. Phys. Chem.* **1993**, *97*, 13126. (b) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708. (c) Jones, W. E.; Chen, P.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 387. (d) Castellano, F. N.; Heimer, T. A.; Tandhasetti, M. T.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041. (e) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1994**, *98*, 7415. (f) Barigelletti, F.; Juris, A.; Balzani, V.; Belsler, P.; von Zelewky, A. *J. Phys. Chem.* **1987**, *91*, 1095. (g) Vining, W. J.; Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1985**, *89*, 1095.
- (10) (a) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967. (b) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4303. (c) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877. (d) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3002. (e) Danielson, E.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1305. (f) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231. (g) Mandal, K.; Pearson, T. P. C.; Krog, W. P.; Demas, J. N. *J. Am. Chem. Soc.* **1983**, *105*, 701. (h) Crosby, G. A.; Watts, R. J.; Carstens, D. H. W. *Science* **1970**, *170*, 1195. (i) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647. (j) Demas, J. N. *J. Chem. Educ.* **1983**, *60*, 803. (k) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834. (l) Hager, G. P.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031. (m) Crosby, G. A.; Elfring, J. *J. Phys. Chem.* **1976**, *80*, 2206. (n) Hipps, K. W.; Crosby, G. A.; *J. Am. Chem. Soc.* **1975**, *97*, 7042.
- (11) Ford, W. E.; Calvin, M. *Chem. Phys. Lett.* **1980**, *76*, 105. (b) Riesen, H.; Krausz, E. R. *J. Chem. Phys.* **1993**, *99*, 7614.
- (12) (a) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526. (b) Chang, Y. J.; Xiaobing, X.; Soo-Chang, Y.; Anderson, D. R.; Orman, L. K.; Hopkins, J. B. *J. Phys. Chem.* **1990**, *94*, 729. (c) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (d) 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. (e) Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643.
- (13) (a) Maruszewski, K.; Bajdor, K.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1995**, *99*, 6286. (b) Van Houten, J.; Watts, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 4853. (c) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 106. (d) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (e) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (f) Clark, R. J. H.; Turtle, P. C.; Strommen, D. P.; Streusand, B.; Kincaid, J. R.; Nakamoto, K. *Inorg. Chem.* **1977**, *16*, 84.
- (14) (a) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (b) Freed, K. F. *Top. Curr. Chem.* **1972**, *31*, 105. (c) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. (d) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (e) Bixon, M.; Jortner, J. *J. Chem. Phys.* **1968**, *48*, 715.

$$\ln[F(\text{calc})] = -1/2 \ln \left[\frac{\hbar\omega_M E_0}{(1000 \text{ cm}^{-1})^2} \right] - S_M - \frac{\gamma E_0}{\hbar\omega_M} + \left(\frac{\gamma + 1}{\hbar\omega_M} \right)^2 \left[\frac{(\Delta\bar{\nu}_{0,1/2})^2}{16 \ln 2} \right] \quad (4b)$$

$$\gamma = \ln \left(\frac{E_0}{S_M \hbar\omega_M} \right) - 1 \quad (4c)$$

depends on the square of the vibrational overlap integral between the initial $\nu_M^* = 0$ level in the excited state and the acceptor vibrational level in the ground state, ν_M . This is the origin of the energy gap term, $\gamma E_0/\hbar\omega_M$, in eq 4b. The vibrational overlap integral is a quantitative measure of the coincidence of the two states along the normal coordinate. The transition between states must occur with energy conservation. The difference between the initial excited-state energy and the energy of the acceptor level, $S_M \hbar\omega_M$, appears in the ground state in coupled low-frequency vibrations and in the solvent. These are included in the term containing the bandwidth, $\Delta\bar{\nu}_{0,1/2}$, in eq 4b. $\Delta\bar{\nu}_{0,1/2}$ includes low-frequency vibrations treated classically ($\chi_{i,L}$) and the solvent reorganizational energy (χ_o). E_0 is related to the 0–0 energy, $E(0-0)$, by eq 5. The relationship between k_{nr} and E_0 in eq 4 has been shown to be valid for MLCT decay in many cases.^{15,16}

$$E(0-0) = E_0 + \frac{(\Delta\bar{\nu}_{0,1/2})^2}{16 \ln 2 k_B T} \quad (5)$$

Since the term linear in E_0 is the most important one in eq 4, the approximation in eq 6 is typically found to hold.^{14a,16} The

$$\ln \tau^{-1} \sim \ln k_{nr} \approx - \frac{\gamma E_0}{\hbar\omega_M} \quad (6)$$

acceptor ligand appears in this relationship in two ways. One is the energy gap. The other is the extent of excited-state distortion as measured by ΔQ_e . ΔQ_e appears in S_M (eq 3) which appears in γ . As noted above, these parameters dictate the magnitude of vibrational wave function overlap between $\nu_M^* = 0$ levels in the excited state and $\nu_M = 0, 1, 2, \dots$ levels in the ground state. In the limit that the energy gap law is valid, overlap increases as E_0 decreases. Overlap also increases as S_M increases.

The dependence of k_{nr} on E_0 and S_M has been verified experimentally. For example, the dependence on energy gap has been demonstrated in the two series $[\text{Os}(\text{phen})(\text{L})_4]^{2+}$ (phen is 1,10-phenanthroline) and $[\text{Os}(\text{bpy})(\text{L})_4]^{2+}$, where the energy gap was varied by changes in the nonchromophoric ligands L.^{14a,17} A role for ligand rigidity and S_M has been found in comparing the two ligands as acceptors. For example, $[\text{Os}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{phen})_3]^{2+}$ have comparable energy gaps ($E_0 \sim 13\,400 \text{ cm}^{-1}$), but k_{nr} for the bipyridine complex ($1.6 \times 10^7 \text{ s}^{-1}$) is approximately four times that of the phenanthroline complex ($3.8 \times 10^6 \text{ s}^{-1}$) in acetonitrile at 298 K.¹⁸ From a Franck–Condon analysis of emission spectra, $S_{\text{bpy}} > S_{\text{phen}}$

Table 1. Ground- and Excited-State Parameters for Ru^{II} and Os^{II} Polypyridyl Complexes at 298 K

complex ^a	λ_{abs} (nm)	λ_{em} (nm)	E_{em} (cm ⁻¹)	τ (ns)	ref
[Ru(bpy) ₃] ²⁺	452	615	16 300	1100	26
[Ru(dmb)(bpy)(COOEt) ₂ (dpp)] ²⁺	479	678	14 700	788	2p
[Ru(dmb)(bpy)(COOEt) ₂ (dpq)] ²⁺	511	790	12 600	29	29b,c
[Ru(dmb)(bpy)(COOEt) ₂ (dpb)] ²⁺	547	>850	<11 800	98	29a,c
[Os(bpy) ₃] ²⁺	658	746	13 400	60	17
[Os(tpy) ₂] ²⁺	657	718	13 900	296	17
[Os(tpy) ₂] ²⁺	668	736	13 600	236	21
[Os(tpy) ₂] ²⁺	692	751	13 300	266	21
[Os(bpy) ₂ (bbpe)] ²⁺	668	810	12 300	58	19
[(bpy) ₂ Os(bbpe)Os(bpy) ₂] ⁴⁺	682	>850	<11 800	52	19
[Ru(bpy) ₂ (dpp)] ²⁺	464	660	15 200	226	30
[Ru(bpy) ₂ (dpp')] ²⁺	466	678	14 700	1214	31
[Ru(bpy) ₂ (dpq)] ²⁺	516	766	13 100	71	30
[Ru(bpy) ₂ (dpq')] ²⁺	536	828	12 100	327	31

^a Complexes in deaerated acetonitrile except where noted. ^b In deaerated 4:1 ethanol:methanol (v/v).

because of enhanced rigidity in phenanthroline as the acceptor arising from the chemical link between the pyridyl rings.

An additional effect has been identified in the bridged complex $\{[\text{Ru}(\text{dmb})_2]_2(\text{bbpe})\}^{4+}$ (bbpe is 1,2-bis(4-(4'-methyl)-2,2'-bipyridyl)ethene).¹⁹ The value of k_{nr} in 4:1 ethanol:methanol at 157 K ($6.6 \times 10^5 \text{ s}^{-1}$) is much less than in $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^{2+}$ ($9.6 \times 10^6 \text{ s}^{-1}$) even though the energy gaps are comparable. Spectral fitting shows that S_M decreases from 0.72 for $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^{2+}$ to 0.38 in the bbpe-bridged complex. The decrease in S_M decreases excited/ground state vibrational overlap. S_M is smaller when bbpe is the acceptor ligand because the excited electron is delocalized over a larger molecular framework. This decreases displacement changes in the local C–C and C–N bonds. Ligand delocalization contributes to the fact that $[\text{Ru}(\text{dmb})_2(\text{bbpe})]^{2+}$ has a longer lifetime (1150 ns) than $[\text{Ru}(\text{dmb})_3]^{2+}$ (950 ns in acetonitrile at 298 K) even though the energy gap in $[\text{Ru}(\text{dmb})_2(\text{bbpe})]^{2+}$ is much smaller ($14\,600 \text{ cm}^{-1}$ compared to $16\,350 \text{ cm}^{-1}$). Recently, Schmehl *et al.* observed a similar effect in $[\text{Ru}(\text{dmb})_2(\text{bphb})]^{2+}$ and $\{[(\text{dmb})_2\text{Ru}]_2(\text{bphb})\}^{4+}$, where bphb is the phenyl-bridged ligand 1,4-bis(4-methyl-2,2'-bipyridin-4-yl)benzene.²⁰

We report here a brief survey of the literature which suggests that these are general effects. Data relevant to this issue are summarized in Table 1. The structures of the ligands are shown in Figure 1.

Analysis

Care must be taken in interpreting the lifetime data in Table 1. In Ru^{II} complexes, contributions to k_{nr} come in varying degrees from thermal population and decay through low-lying dd states and upper MLCT states.^{8,18} Analysis of lifetimes based on the energy gap law is valid only for nonradiative decay from the lowest MLCT state or states. Contributions to k_{nr} from competing thermally activated processes can be assessed by temperature-dependent lifetime measurements, but even in the absence of these data there are revealing trends in the data in Table 1.

There are clear-cut examples of the delocalization effect in the series $[\text{Ru}(\text{dmb})(\text{bpy})(\text{COOEt})_2(\text{LL})]^{2+}$, where LL is 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq), and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb). As the number of rings in the dpp, dpq, or dpb acceptor ligands is increased, the energy gap (as approximated by E_{em}) decreases. The

- (15) (a) Barqawi, K. R.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 47. (b) Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849.
 (16) (a) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.
 (17) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.
 (18) Lumpkin, R. S.; Kober, E. M.; Worl, L.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1990**, *94*, 239.

- (19) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyd, S.; Jones, W. E.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473.
 (20) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198.

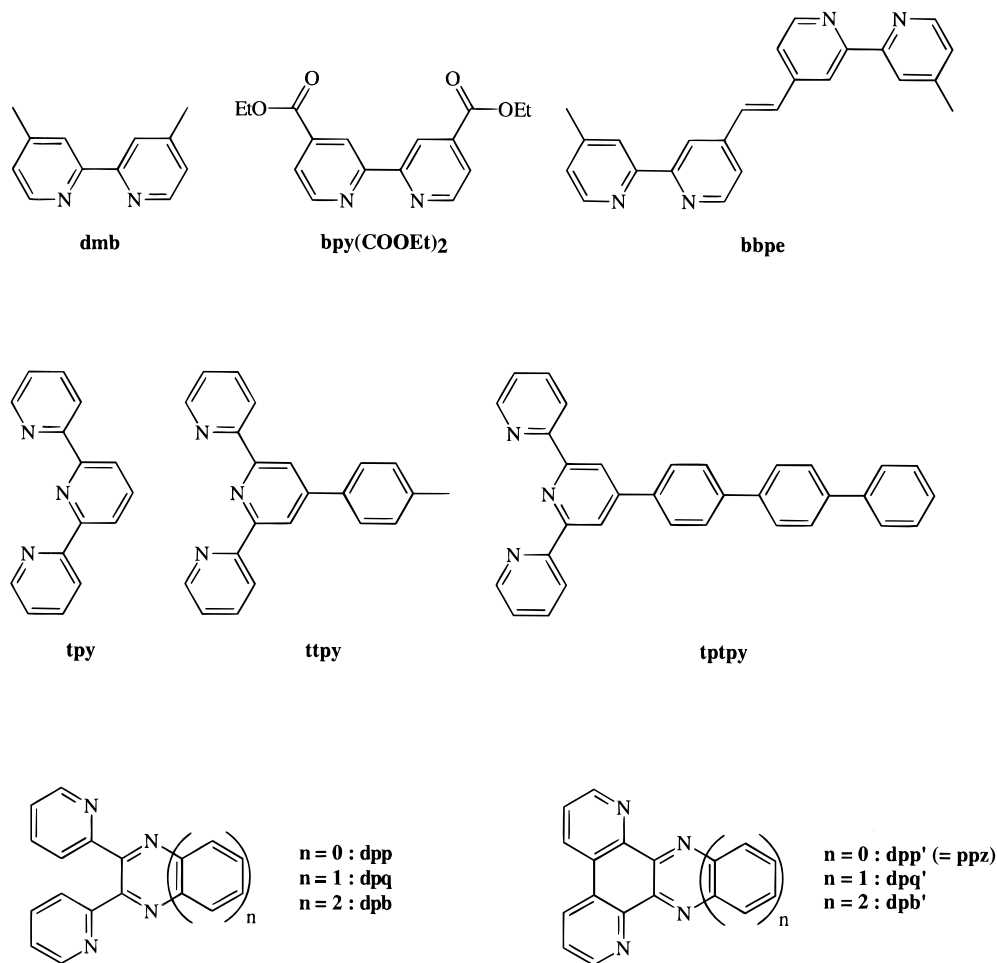


Figure 1. Ligand structures.

decrease in the energy gap occurs because of stabilization of the lowest π^* acceptor level as shown by electrochemical measurements. The $\text{Ru}^{\text{III/II}}$ potentials for the three are nearly constant at 1.44–1.47 V (versus SCE, 0.1 M $[\text{N}(n\text{-C}_4\text{H}_9)_4](\text{PF}_6)$ in acetonitrile) while the ligand-based reduction potentials are -0.96 V (dpp), -0.75 V (dpq), and -0.59 V (dpb). The excited-state lifetime does decrease from LL = dpp to LL = dpq (although less than expected based solely on the energy gap), but in a comparison of dpq and dpb as acceptor ligands, the excited-state lifetime actually increases from 29 to 98 ns even though the energy gap decreases by ~ 1000 cm^{-1} . In these complexes, the MLCT excited states are relatively low in energy. Ligand loss photochemistry, which usually accompanies non-radiative decay by thermal activation to dd states, is either of low efficiency or not observed, and dd states presumably play a negligible role in dictating the magnitude of τ .

Another example is shown in the Os(II) complexes containing terpyridyl derivatives as the acceptor ligands. In these ligands there are three acceptor rings compared to two for bipyridine. $[\text{Os}(\text{tpy})_2]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ have comparable energy gaps, but the terpyridine complex exhibits a substantially longer lifetime (296 ns compared to 60 ns).¹⁷ In a comparison of $[\text{Os}(\text{ttpy})_2]^{2+}$ and $[\text{Os}(\text{tppy})_2]^{2+}$, the latter has an energy gap 270 cm^{-1} smaller than the former yet exhibits a longer lifetime (266 ns versus 236 ns).²¹ The Os(II) complexes incorporating bbpe as an acceptor ligand provide another example. $[\text{Os}(\text{bpy})_2$

(bbpe)]^{2+*} has an energy gap that is ~ 1000 cm^{-1} smaller than $[\text{Os}(\text{bpy})_3]^{2+*, but their lifetimes are nearly the same. $[(\text{bpy})_2\text{Os}(\text{bbpe})\text{Os}(\text{bpy})_2]^{4+* emits even further into the red ($< 11\,800$ cm^{-1}) but has a comparable lifetime.¹⁹ Because $10Dq$ is $\sim 30\%$ larger for Os(II) compared to Ru(II), excited-state behavior for Os(II) complexes tends to be free of complicating features arising from dd states.²²$$

A combination of rigidity and delocalization may account for the enhanced lifetimes of $[\text{Ru}(\text{bpy})_2(\text{dpp}')]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{dpq}')]^{2+}$ compared to $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{dpq})]^{2+}$. Delocalization plays a role as evidenced by the decrease in emission energies, but the bipyridine versus phenanthroline comparison mentioned above suggests that the additional bond linking the ring systems in dpp' and dpq' may play a role as well.

There are additional examples in the literature where extended π systems and delocalization in the acceptor ligand appear to play a significant role. Examples include (Figure 2) i-biq,²³ dpop,²⁴ HAT,²⁵ dmch,²⁶ dppz,²⁷ and the series tpy(phenyl)_ntpy ($n = 0, 1, 2$).²⁸ A proper accounting must await a more

(21) (a) Beley, M.; Collin, J.; Sauvage, J.; Sugihara, H.; Heisel, F.; Miehé, A. *J. Chem. Soc., Dalton Trans.* **1991**, 3175. (b) Beley, M.; Chodorowski, S.; Collin, J.; Sauvage, J.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543.

(22) (a) Jorgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: London, 1962; p 114. (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614.

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

(24) (a) Ruminski, R. R.; Servies, D.; Jacquez, M. *Inorg. Chem.* **1995**, *34*, 3358. (b) Ruminski, R. R.; Freiheit, D.; Johnson, J. E. B. *Inorg. Chim. Acta* **1994**, *224*, 27.

(25) (a) Buyl, F. d.; Mesmaeker, A. K.; Tossi, A. *J. Photochem. Photobiol., A: Chem.* **1991**, *60*, 27. (b) Sahia, R.; Rillema, D. P.; Shaver, R.; Van Wallendael, S.; Jackman, D. C.; Boldaji, M. *Inorg. Chem.* **1989**, *28*, 1022.

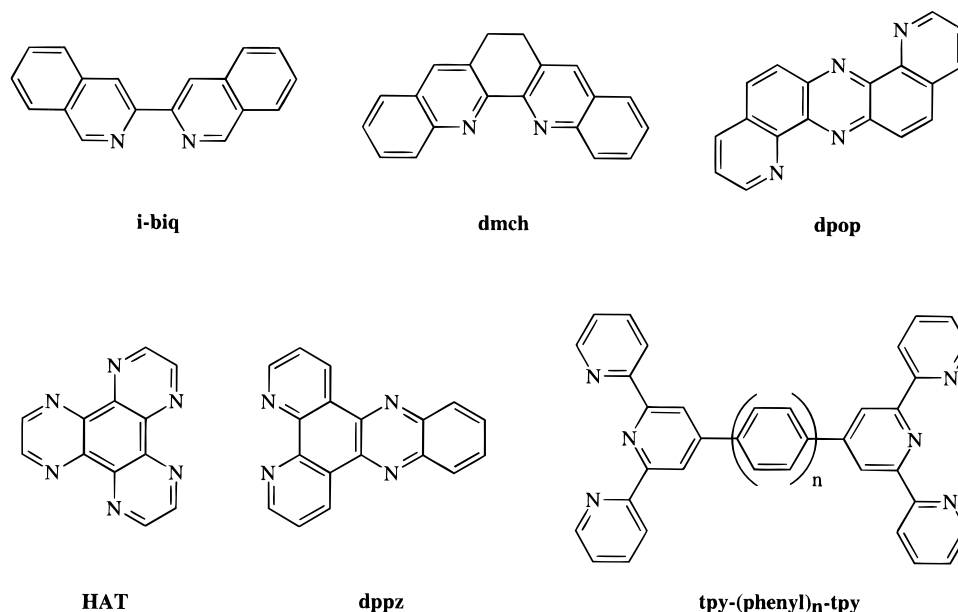


Figure 2. Ligand structures where delocalization appears to play a significant role.

comprehensive analysis including spectral fitting and temperature-dependent lifetime measurements for the Ru(II) complexes.

Conclusions

On the basis of our observations, there are important implications for nonradiative decay and for the design of MLCT excited states. They point out that the energy gap law must be applied with care. As suggested by eq 5, $\ln k_{nr}$ and $\ln \tau^{-1}$ may vary with energy gap, but they also depend on γ and S_M (eqs 4). Within the series $[\text{Os}(\text{phen})(\text{L})_4]^{2+*}$ and $[\text{Os}(\text{bpy})(\text{L})_4]^{2+*}$, S_M has been found to vary linearly with E_0 .^{15a,16a,17} As the structure of the acceptor ligand is varied, the dependence of S_M on E_0 will vary as well. Each acceptor ligand should have its own energy gap dependence.

If applied systematically, the rigidity and delocalization effects offer new possibilities for the design of controlled excited-state properties. For example, we recently reported a synthetic approach to "black" MLCT chromophores which absorb appreciably throughout much of the near UV–vis.²⁹ The energy gaps of the excited states formed upon MLCT excitation are small, e.g. $E_{em} < 11\,800\text{ cm}^{-1}$ for $[\text{Ru}(\text{dmb})(\text{bpy}(\text{COOEt})_2)(\text{dpb})]^{2+*}$, which would normally lead to short lifetimes. The

combination of both rigidity and delocalization in dpb as the acceptor ligand, however, leads to an excited state lifetime ($\tau = 98\text{ ns}$ in acetonitrile at 298 K) long enough for either intra- or intermolecular electron or energy transfer to compete with excited-state decay.

Acknowledgment. Financial support from the Australian Research Council, Fondecyt-CHILE (Grant 1940577), Conicyt-CHILE (Grant 2950063), and the U.S. Department of Energy (Grant DE-FG05-86ER13633) is gratefully acknowledged. Travel between the laboratories at PUC and UNC (B.L. and R.L.) has been supported by the U.S. National Science Foundation (Grant INT-9123215) and Conicyt. Travel between the laboratories at JCUNQ and UNC (J.A.T. and P.A.A.) has been supported by the U.S. National Science Foundation (Grant INT-9015262) and the Australian Department of Industry, Science, and Technology within the Australia-U.S. Bilateral Science and Technology Program.

IC950961S

- (26) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 2175.
 (27) (a) Amouyal, E.; Homsy, A.; Chambron, J.; Sauvage, J. *J. Chem. Soc., Dalton Trans.* **1990**, 1841. (b) Hartshorn, R. M.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 5919.
 (28) (a) Collin, J.; Guillerez, S.; Sauvage, J.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230. (b) Collin, J.; Guillerez, S.; Sauvage, J. *J. Chem. Soc., Chem. Commun.* **1989**, 776.

- (29) (a) Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3863. (b) Anderson, P. A. Ph.D. Thesis, James Cook University of North Queensland, Australia, 1995. (c) Anderson, P. A.; Keene, F. R.; Loeb, B.; Lopez, R.; Meyer, T. J.; Strouse, G. F.; Treadway, J. A. Manuscript in preparation.
 (30) (a) Molnar, S. M.; Neville, K. R.; Jensen, G. E.; Brewer, K. J. *Inorg. Chim. Acta* **1993**, *206*, 69. (b) Wallace, A. W.; Murphy, W. R.; Petersen, J. D. *Inorg. Chim. Acta* **1989**, *166*, 47.
 (31) (a) Lopez, L. Licentiate and Chemist Degree Thesis, Pontificia Universidad Catolica de Chile, 1994. (b) Loeb, B. L.; Lopez, R.; Lopez, L.; Treadway, J. A.; Claude, J. P.; Meyer, T. J. Work in progress.