# Luminescent Ruthenium(II) Bipyridyl−Phosphonic Acid Complexes: pH Dependent Photophysical Behavior and Quenching with Divalent Metal Ions

**Marco Montalti, Seema Wadhwa, Won Y. Kim, Rachael A. Kipp, and Russell H. Schmehl\***

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

The synthesis, redox behavior, and photophysical properties of a series of Ru(II) bipyridyl complexes having diimine ligands with phosphonate and phosphonic acid substituents are presented. The phosphonate-containing ligands examined include diethyl 4-(2,2′-bipyrid-4-yl)benzylphosphonate (bpbzp), diethyl 4-(2,2′-bipyrid-4-yl)-phenylphosphonate (bppp), and 4,4′-(diethyl phosphonato)-2,2′-bipyridine (bpdp), and the $[(bpy)_2Ru(L)](PF_6)_2$ complexes of both the diethyl phosphonate and the phosphonic acid were prepared. The Ru(III/II) potentials are more positive for the phosphonate complexes than for the phosphonic acids, and the first reduction is localized on the phosphonate-containing ligand for the bppp and bpdp complexes. The first reduction of the phosphonic acid complexes is at more negative potentials and cannot be distinguished from bpy reduction. For the bppp and bpdp complexes luminescence arises from a $Ru(d\pi) \rightarrow$ bpy-phosphonate $(\pi^*)$ MLCT state; the phosphonic acid complexes luminesce at higher energies from a MLCT state not clearly isolated on one ligand. Iron(III) and copper(II) complex with and very efficiently quench the luminescence of all the phosphonic acid complexes in nonaqueous solvents. The quenching mechanism is discussed on the basis of luminescence decay and picosecond transient absorption measurements.

## Introduction

There has been considerable recent effort to prepare clusters of chromophores that can serve as light-harvesting arrays or extended chromophoric systems for various applications (such as light electrochromic displays).[1] Visible light harvesting ensembles have been prepared using a variety of chromophores including porphyrins, metalloporphyrins and transition metal complexes having metal-to-ligand charge-transfer excited states.[2−6] Most arrays of this type have chromophores interconnected via covalent linkages. The chromophores exist either as substituents on a polymer backbone or as monomeric units of a synthetic polymer. In an effort to examine noncovalently linked arrays of transition metal complex chromophores, we have prepared diimine ligands with phosphonic acid substituents.[7] Complexes having multiple phosphonic acid substituents can, in principle, form arrays via complex-forming interactions with ions in solution capable of binding multiple phosphonic acids (eq 1 for a linear oligomer). Recent work by several groups, most notably Mallouk[8] and Thompson,[9] has shown that multilayer arrays of organic bis-phosphonic acids can be prepared on surfaces capable of binding the acids.

$$n[(H_2O_3P\text{-bpy})_2Ru(bpy)]^{2+} + nM^{q+} \rightarrow$$
$$\{[(O_3P\text{-bpy})Ru(bpy)(bpy\text{-}PO_3M)]\}_n^{(2+q)+} \quad (1)$$
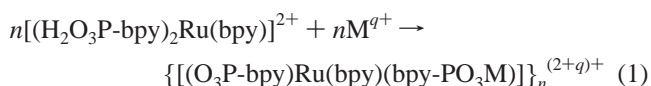
To employ phosphonic acid complex layered arrays in light harvesting (or sensitization), it is useful to assess both the strength of the ionic association complexes formed and the

(1) (a) Fox, M. A.; Watkins, D. M.; Jones, W. E., Jr. *Chem. Eng. News* **1993,** *71,* 38−48. (b) Wasielewski, M. R. *Chem. Rev.* **1992,** *92,* 435. (c) Also see: Leising, G.; Tasch, S.; Graupner, W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolde, J. R., Eds.; M. Dekker: New York, 1998; p 847. (d) Chen, L. X.; Jager, W. J. H.; Niemczyk, M. P.; Wasielewski, M. R. *J. Phys. Chem. A* **1999,** *103,* 4341−51. (e) Kim, S.; Jackiw, J.; Robinson, E.; Schanze, K. S.; Reynolds, J. R.; Baur, J.; Rubner, M. F.; Boils, D. *Macromolecules* **1998,** *31* (4), 964−974.

(2) (a) Bothner-By, A. A.; Dadok, J.; Johnson, T. E.; Lindsey, J. S. *J. Phys. Chem.* **1996,** *100,* 17551−17557. (b) Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, C. H., III; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998,** *120,* 10001−10017. (c) Strachan, J.-P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997,** *119,* 11191−11201.

(3) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Alternative Fuels and the Environment*; Sterrett, F. S., Ed.; Lewis Publishers: Boca Raton, FL, 1995; p 125−139. (b) Gust, D.; Moore, T. A.; Moore, A. L.; Macpherson, A. N.; Lopez, A.; DeGraziano, J. M.; Gouni, I.; Bittersmann, E.; Seely, G. R.; Gao, F.; Nieman, R. A.; Ma, X. C.; Demanche, L. J.; Hung, S.-C.; Luttrull, D. K.; Lee, S.-J.; Kerrigan, P. K. *J. Am. Chem. Soc.* **1993,** *115,* 11141−11152. (c) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994,** *264,* 1105−1111. (d) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995,** *117,* 9461−9472. (e) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995,** *117,* 704−714.

(4) (a) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998,** *31,* 26−34. (b) See: Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991; Chapter 6. (c) De Cola, L.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A.; Seel, C.; Frank, M.; Voegtle, F. *Coord. Chem. Rev.* **1991,** *111,* 255−260.

(5) (a) Jones, W. E., Jr.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993,** *115,* 7363−7373. (b) Younathan, J. N.; Jones, W. E., Jr.; Meyer, T. J. *J. Phys. Chem.* **1991,** *95,* 488−492. (c) Baxter, S. M.; Jones, W. E., Jr.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991,** *111,* 47−71.

(6) (a) Shaw, J. R.; Ryu, C. K.; Sadler, G. S.; Wacholtz, W. F.; Schmehl, R. H. *New J. Chem.* **1996,** *20,* 749−758. (b) Wang, R.; Liang, Y.; Schmehl, R. H. *Inorg. Chim. Acta* **1994,** *225,* 275.

(7) Gratzel and co-workers have reported the preparation of these ligands, metal diimine complexes, and application to the preparation of chemically modified surfaces for the purposes of semiconductor sensitization. See: Graetzel, M.; Kohle, O.; Nazzeruddin, M. K.; Pechy, P.; Royzinger, F. P.; Ruile, S.; Zakeeruddin, S. M. PCT Int. Appl. WO 95 29,924 (Cl. CO7F9/58), 9 Nov 1995, Appl. 94/IB88, 2 May 1994, 52 pp.

(8) (a) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992,** *25,* 420. (b) Kaschak, D. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996,** *118,* 4222. (c) Mallouk, T. E.; Keller, S. W.; Kim, H.-N. *J. Am. Chem. Soc.* **1994,** *116,* 8817.

(9) (a) Vermeulen, L. A.; Snover, J. L.; Sapochak, L. S.; Thompson, M. E. *J. Am. Chem. Soc.* **1993,** *115,* 11767−11774. (b) Byrd, H.; Snover, J. L.; Thompson, M. E. *Langmuir* **1995,** *11,* 4449. (c) Thompson, M. E.; Snover, J. L.; Byrd, H. *Chem. Mater.* **1996,** *8,* 1490.

**Scheme 1**
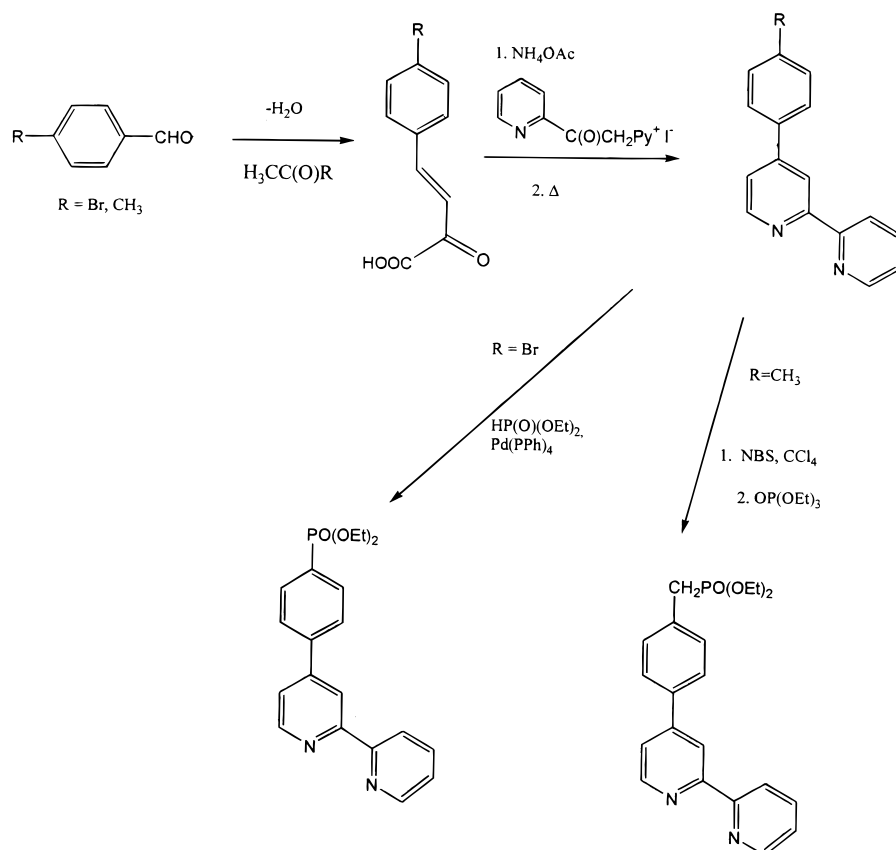


efficiency of interchromophore energy transfer. This work presents the synthesis and characterization of three phosphonate ligands and corresponding Ru(II) complexes having a single phosphonate (or phosphonic acid) ligand. In addition, association
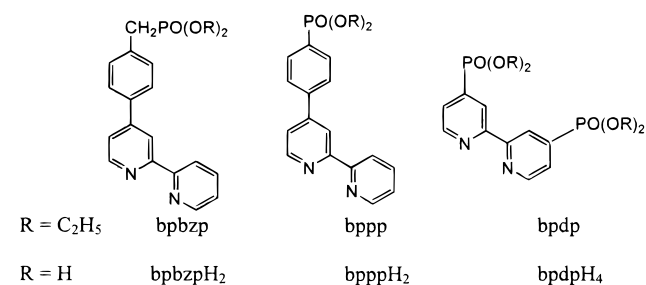


of the luminescent complexes with metal ions capable of quenching the MLCT luminescence is presented. The results indicate that binding constants of many divalent metal ions with the phosphonic acid substituents are high enough to form stable complexes in noncoordinatng solvents.

**Results and Discussion**

**A. Synthesis of Ligands and Complexes.** The ligand bpdpH$_4$ was prepared by a modification of a procedure by Penicaud and co-workers;[10] details of the synthesis are given in the Experimental Section. The ligands having a single phosphonic acid substituent were prepared as shown in Scheme 1. These ligands are useful because the preparations employ inexpensive starting materials, the procedures are simple, and the yields are reasonably high. For each monophosphonic acid ligand a *p*-X-benzaldehyde derivative (X = CH$_3$, Br) is initially coupled with

pyruvic acid to yield an intermediate enone. This is then added to acetylpyridine pyridinium iodide in a Hantzsch condensation to produce the 6-carboxy-2,2′-bipyridine, which is decarboxylated thermally.

The ethyl ester of the benzyl phosphonate ligand, bpbzp, is prepared via a Michaelis−Arbuzov reaction. The resulting acid, bpbzpH$_2$, is obtained by hydrolysis of the ethyl ester, bpbzp, with trimethylsilyl bromide in dry acetonitrile following complexation with Ru(II).

The ethyl ester, bppp, is prepared by Pd-catalyzed coupling of diethyl phosphite with 4-(*p*-bromophenyl)-2,2′-bipyridine in dry THF. Hydrolysis of the ethyl ester of the phosphonate was accomplished with trimethylsilyl bromide following coordination of the ligand to Ru(II).

For each of the ligands, luminescent Ru(II) complexes are prepared by reaction of an excess of the ethyl ester of each ligand with [(bpy)$_2$RuCl$_2$] in ethanol using established procedures. The resulting [(bpy)$_2$Ru(L)](PF$_6$)$_2$ complexes were characterized by $^1$H NMR, IR, and cyclic voltammetry. Elemental analytical data was obtained for the phosphonate ester ligands and Ru(II) complexes. The acid complexes, prepared by hydrolysis of the esters, were assumed to be pure if no ethyl (−CH$_2$− or −CH$_3$) resonances remained in the $^1$NMR spectrum.

**B. Redox Behavior of the Complexes.** Cyclic voltammograms in acetonitrile of the complexes having the ester ligands exhibit a single, reversible, one-electron oxidation wave and two reversible reductions. The potentials cited in Table 1 refer to the overall charge of the complex before and after reduction. The potential of the oxidation is more positive than that of the parent complex [(bpy)$_3$Ru](PF$_6$)$_2$, particularly for the complex

(10) Penicaud, V.; Odobel, F.; Bujoli, B. *Tetrahedron Lett.* **1998**, *39* (22), 3689−3692.

**Table 1.** Redox and Room Temperature Spectrophotometric Measurements of Complexes in Solution

| complex | solvent | $\lambda_{max}$, nm (log($\epsilon$)) | $E$(III/II), V[a] | $E$(II/I), V | $E$(I/0), V |
|---|---|---|---|---|---|
| [(bpy)$_2$Ru(bpbzp)]$^{2+}$ | CH$_3$CN | 457 | 1.18 | −1.4 | −1.6 |
| [(bpy)$_2$Ru(bpbzpH$_2$)]$^{2+}$ | CH$_3$CN | 456 | 1.17 | −1.4 | |
| [(bpy)$_2$Ru(bppp)]$^{2+}$ | CH$_3$CN | 458 | 1.27 | −1.26 | −1.48 |
| [(bpy)$_2$Ru(bpppH$_2$)]$^{2+}$ | CH$_3$CN | 458 | 1.20 | −1.42 | −1.57 |
| [(bpy)$_2$Ru(bpdp)]$^{2+}$ | CH$_3$CN | 456 | 1.28 | −1.11 | −1.54 |
| [(bpy)$_2$Ru(bpdpH$_4$)]$^{2+}$ | H$_2$O | 456 | 1.05[b] | −1.45 | −1.65 |

[a] Potentials vs SSCE at Pt with tetraethylammonium perchlorate electrolyte, unless otherwise specified. [b] Versus SSCE in 1 M H$_2$SO$_4$ at a glassy carbon electrode.

of bpdp. The bipyridyl phosphonate esters serve as strong electron-withdrawing groups, and the behavior mimics that of complexes having bipyridines with carboxy ester substituents in the 4 and 4′ positions.[11] One-electron reduction of tris diimine complexes of Ru(II) has been thoroughly investigated and is known to involve reduction of one of the coordinated ligands.[12] The first reductions of the bpdp and bppp complexes are at significantly more positive potentials than the first reduction of [(bpy)$_3$Ru](PF$_6$)$_2$ and are clearly localized on the phosphonate-containing ligand. The first reduction of the bpbzp complex is less positive, and it is not clear whether the reduction is localized on the phosphonate ester ligand or the bpy.
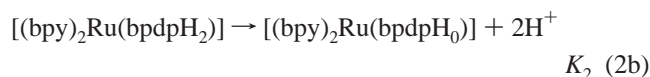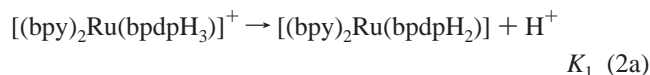
The redox behavior of the hydrolyzed ester complexes is somewhat more complex. Since the phosphonic acids undergo dissociation to some degree, the behavior must be influenced by the pH of the solvent. We have not explored this in detail, and the potentials given in Table 1 are for the isolated complexes dissolved in unbuffered solvent. The principal difference between these complexes and the phosphonate ester complexes is that the first reduction is at significantly more negative potentials for the complexes of bppp and bpdp. In addition, the Ru(III/II) potentials for the bpppH$_2$ and bpdpH$_4$ are more negative than the ester complexes. Very likely the phosphonic acids are partially dissociated in solution (vide infra) and reduction of the bipyridine containing the acid therefore occurs at more negative potentials due to the partial negative charge on the ligand. The potential for the bpdpH$_4$ complex was measured in a strongly acidic aqueous solution, and it is surprising that the potential is very different from that of the ester since the phosphonic acid complex should be fully protonated in the sulfuric acid solution. It is unlikely that solvation effects account for the apparent discrepancy since the bipyridine-localized one-electron-reduction potentials follow the same trend as that followed by the bppp complexes in CH$_3$CN.

**C. Photophysical Behavior of the Complexes. Absorption and Luminescence in Unbuffered Solutions and Low-Temperature Matrixes.** Absorption maxima for the metal-to-ligand charge transfer (MLCT) absorption of the complexes is given in Table 1 and luminescence data for room temperature solutions and frozen matrixes is presented in Table 2. The most striking change in behavior between the phosphonate ester and acid complexes is for [(bpy)$_2$Ru(bpdp)]$^{2+}$ and the corresponding acid, where a blue shift of more than 50 nm is observed in the emission spectrum upon hydrolysis of the ester. On the basis of the localization of the one-electron-reduction potential, the MLCT transition for the bpdp complex is Ru(d$\pi$) to bpdp($\pi$*)

localized. The difference between the bpdp complex and the bpdpH$_4$ results from the large decrease in the electron-accepting ability of the bpdp ligand upon hydrolysis (as evidenced by the large negative shift in the E(II/I) potential). The change reflects an increase in the energy of the lowest bpdp $\pi$* orbital following hydrolysis and a concomitant increase in the emission energy of the Ru(d$\pi$) to bpdp ($\pi$*) MLCT state (the observed MLCT transition may also have Ru (d$\pi$) to bpy ($\pi$*) character). Very similar behavior is observed in the photophysical properties of [(bpy)$_2$Ru(L)]$^{2+}$ complexes having carboxy ester substituents in the 4,4′ or 5,5′ positions of the bipyridine.[11,13] A less pronounced emission spectral change is observed for the bppp complex, where the effect of phosphonate ester hydrolysis on the $\pi$* energy of the ligand is much smaller. Phosphonate hydrolysis has essentially no effect on the luminescence behavior of the bpbzp complex. Luminescence lifetimes and emission quantum yields for the complexes are also given in Table 2. The data are typical of $^3$MLCT emission from Ru(II) diimine complexes, with calculated radiative decay rate constants ($\phi_{em}/\tau_{em}$) of 5−10 × 10$^4$ s$^{-1}$.[12]

The relative emission maxima of 77 K luminescence spectra mirror the room temperature luminescence behavior (Table 2). In addition, the low-temperature spectra exhibit vibrational structure with 1300−1400 cm$^{-1}$ spacings characteristic of Ru-(II) diimine complexes. Luminescence lifetimes for both the phosphonate ester complexes and phosphonic acids at 77 K are approximately 5 $\mu$s.

**Effect of pH on Spectra of the Phosphonic Acid Complexes.** Titration of [(bpy)$_2$Ru(bpppH$_2$)]$^{2+}$ yields two clear acid dissociations with p$K$ values of ∼2 and 6.3. However, titration of [(bpy)$_2$Ru(bpdpH$_4$)]$^{2+}$ with base yields only two resolvable endpoints. The first endpoint is reached upon the addition of 1 equiv of base and has a midpoint pH of approximately 1; the second endpoint requires 2 equiv and has a midpoint pH of 6. The result suggests that the isolated form of the bpdpH$_4$ complex is [(bpy)$_2$Ru(bpdpH$_3$)]$^+$ with measurable acid dissociations involving one and two protons, respectively (eqs 2a,b). The p$K$ values measured are comparable to those reported for alkyl and aryl phosphonic acids, although in aqueous solution the first p$K_a$ is reported to be below 1.[14]

$$[(bpy)_2Ru(bpdpH_3)]^+ \rightarrow [(bpy)_2Ru(bpdpH_2)] + H^+$$
$$K_1 \quad (2a)$$

$$[(bpy)_2Ru(bpdpH_2)] \rightarrow [(bpy)_2Ru(bpdpH_0)] + 2H^+$$
$$K_2 \quad (2b)$$

The absorption and luminescence behavior of the bpdpH$_4$ and the bpppH$_2$ complexes is pH dependent in aqueous solutions. Emission spectra of [(bpy)$_2$Ru(bpdpH$_n$)]$^{n-2}$ ($n = 0−4$) at varying pH's are shown in Figure 1. When the pH is raised, the emission maximum shifts to shorter wavelength and the integrated emission intensity increases. Figure 2 shows the pH dependence of the MLCT absorbance at 460 nm and the integrated emission intensity for the bpdpH$_4$ complex. Similar behavior has been observed for complexes of 2,2′-bipyridine-4,4′-dicarboxylic acid in aqueous solution.[15] The spectrophotometric data can be used to determine the ground state p$K$

(11) (a) Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519−7526. (b) DeLaive, P. J.; Whitten, D. G.; Giannotti, C. *Adv. Chem. Ser.* **1979**, *173*, 236−51.

(12) See: Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277 and references therein.

(13) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227−234.

(14) Matczak-Jon, E.; Kurzak, B.; Kafarski, P. *J. Chem. Soc., Dalton Trans.* **1998**, 161.

(15) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187−3189.

**Table 2.** Photophysical Properties of the Complexes in Solution at Room Temperature and Low Temperature Matrixes

| complex | solvent | $E_{em}$, nm, 298 K | $E_{em}$, nm, 77 K[a] | $\tau_{em}$, $\mu s$, 298 K | $\phi_{em}$, 298 K | $\tau_{em}$, $\mu s$, 77 K |
|---|---|---|---|---|---|---|
| $[(bpy)_2Ru(bpbzp)]^{2+}$ | $CH_3CN$ | 624 | 594 | 1.18 | 0.093 | 5.04 |
| $[(bpy)_2Ru(bpbzpH_2)]^{2+}$ | $CH_3CN$ | 620 | 593 | 0.98 | 0.062 | 5.06 |
| $[(bpy)_2Ru(bppp)]^{2+}$ | $CH_3CN$ | 624 | 594 | 1.58 | 0.07 | 5.7 |
| $[(bpy)_2Ru(bpppH_2)]^{2+}$ | $CH_3CN$ | 616 | 590 | 1.33 | 0.065 | 5.7 |
| $[(bpy)_2Ru(bpdp)]^{2+}$ | $CH_3CN$ | 685 | 631 | 0.77 | 0.04 | 4.9 |
| $[(bpy)_2Ru(bpdpH_4)]^{2+}$ | $H_2O$ | 626 | 598 | 1.07 | 0.06 | 4.9 |

[a] Emission maximum in 4:1 ethanol/methanol matrixes.
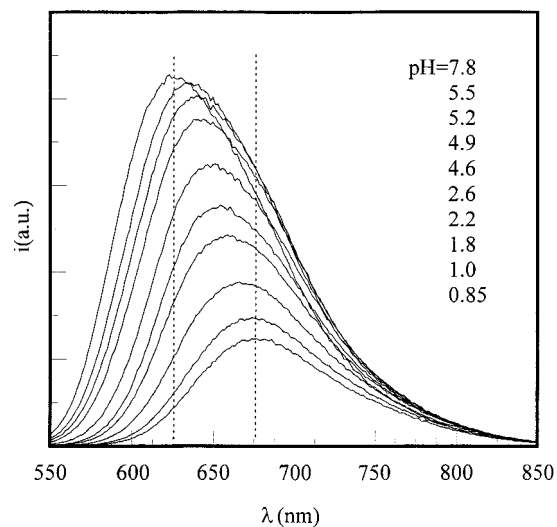


**Figure 1.** Emission spectra of $[(bpy)_2Ru(bpdpH_2)]^{2+}$ (formula for strongly acidic solution) at varying pH's.
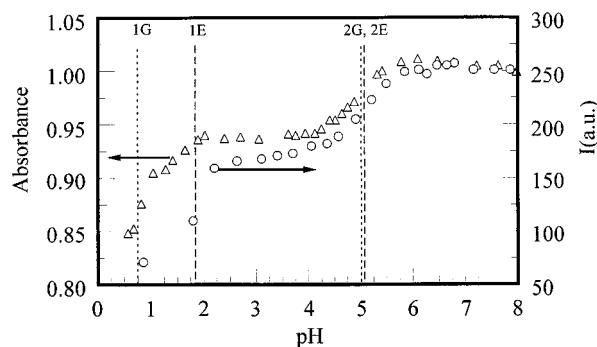


**Figure 2.** pH dependence of 460 nm absorbance and integrated emission intensity for $[(bpy)_2Ru(bpdpH_2)]$ in water. The 1G, 2G, 1E, and 2E lines note the approximate midpoints in the observed spectroscopic changes with pH of the ground (G) and excited (E) states.

values, and the luminescence data are related to excited state acid dissociation. Comparison of ground state and excited state acid dissociation constants is useful because the relative change in the $pK_a$ provides qualitative information on the localization of charge in MLCT states. If the excited state $pK_a$ is higher than the ground state value for the same process, the implication is that the MLCT state is localized on the ligand containing the acidic substituent (the excited state has increased negative charge and is therefore less acidic). Ireland and Wyatt have developed methods for the evaluation of excited state acid dissociation constants from luminescence intensity and lifetime data;[16] using their procedure and recognizing the fact that the bpdpH$_4$ ligand has four titratable protons which are assumed to dissociate in

**Table 3.** Ground and Excited Acid Dissociation Data in Room Temperature Solutions

| complex | ground state p$K$ | emission inflection | $\tau$, $\mu s$ protonated | $\tau$, $\mu s$ unprotonated | p$K$* |
|---|---|---|---|---|---|
| $[(bpy)_2Ru(bpppH_2)]^{2+}$ | | | | | |
| $K_1$ | <2 | 2.35 | 0.493 | 0.549 | 2.4 |
| $K_2$ | 6.3 | 4.8 | 0.549 | 0.477 | 4.7 |
| $[(bpy)_2Ru(bpdpH_4)]^{2+}$ | | | | | |
| $K_1$ | 1.0 | 1.9 | 0.193 | 0.334 | 1.7 |
| $K_2$ | 12.0[a] | 5.1 | 0.334 | 0.443 | 10.1[a] |

[a] The p$K$ value reported is for the two-proton dissociation represented by eq 2b and evaluated using eq 3.

two measurable steps,[17] the value for each $pK_a$ of the excited state can be determined using eq 3 to evaluate the pH at the midpoint of the dissociation (the $N$ of eq 3 is 1 for the single-proton dissociation of eq 2a and 2 for the two-proton dissociation of eq 2b). The lifetime values are experimentally obtained at pH levels well above and well below the midpoint, where $\tau$ is relatively invariant with pH. Values for the measurable ground state and excited state p$K$'s for the bpdpH$_4$ and the bpppH$_2$

$$N\,pH = pK_a^* - \log(\tau_{acid}/\tau_{base}) \tag{3}$$

complexes are given in Table 3.

The data of Figure 2 are complicated by several factors. First, as indicated above, titration results for a solution of the bpdpH$_4$ complex indicate that the isolated form of the complex is $[(bpy)_2Ru(bpdpH_3)](PF_6)$. Given that the first measurable dissociation of the ground state is for the triprotic form of the complex, the value of the first p$K$ reported in Table 3 is for loss of a single proton. From the direct pH titration, the second p$K$ is for dissociation of the third and fourth protons, eq 2b; the measured midpoint in the titration is at pH 6 and thus the p$K$ value is 12. Figure 2 indicates the midpoint of the spectrophotometric titration is at pH 5. This can be explained if it is assumed that spectrophotometric changes are only observed for the first deprotonation of eq 2b and therefore the p$K$ of 5 is explicitly for the dissociation of the third titratable proton (not resolvable in pH measurements). In determining the excited state p$K$ value, we have assumed that intensity changes observed reflect both the third and fourth dissociation processes (eq 3 with $N = 2$).

The results indicate that the first excited state dissociation constants of both complexes, $pK_1^*$, are slightly higher than the ground state $pK_1$, but the second dissociation constant is lower for the excited state. Thus the MLCT excited state of the fully protonated complex is more basic than the ground state, suggesting that the MLCT transition is localized on the bpppH$_2$

(16) Ireland, J. F.; Wyatt, P. A. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

(17) The ground state pH titrations of the complexes of bpdpH$_4$ (4 titratable protons) and bpppH$_2$ are very similar with apparent p$K$ values of ~1.5 and ~6. On the basis of this observation, we have assumed that the dissociation of protons from bpdpH$_4$ occurs in two measurable steps; each p$K$ value for the two phosphonic acid moieties is nearly the same for the bpdpH$_4$ complex.
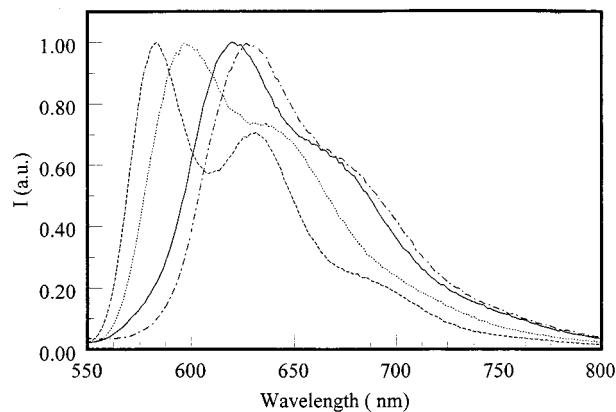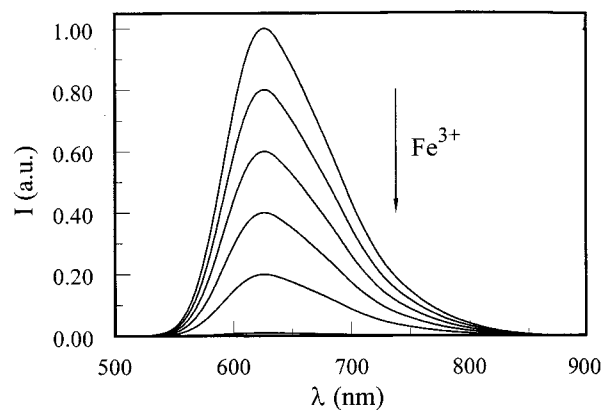
**Figure 3.** Luminescence spectra of $[(bpy)_2Ru(bpdpH_2)]^{2+}$ in 77 K matrixes of 4:1 ethanol/methanol with (---) added base, (•••) no additive, and (—) added acid. The spectrum of the phosphonate, $[(bpy)_2Ru(bpdp)]^{2+}$, is also shown (—•—).
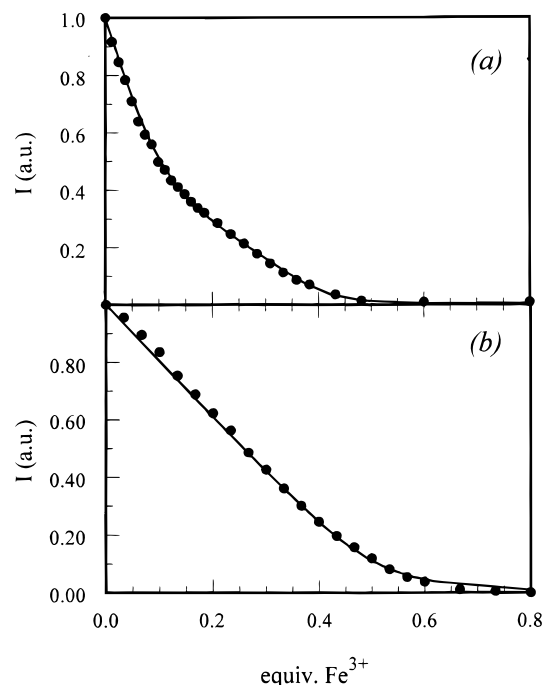


**Figure 4.** Luminescence spectra of $[(bpy)_2Ru(bpppH_2)]^{2+}$ (60 $\mu$M) in $CHCl_3$/MeOH in the presence of increasing amounts of $Fe^{3+}$.

and bpdpH$_4$ ligands. This is consistent with the fact that the luminescence maxima of $[(bpy)_2Ru(bpppH_2)]^{2+}$ and $[(bpy)_2Ru(bpdpH_4)]^{4+}$ are lower in energy in strongly acidic solution, at pH's below p$K_1$*. The smaller dissociation constants for the excited states of the $[(bpy)_2Ru(bpppH)]^+$ and $[(bpy)_2Ru(bpdpH_2)]^+$ complexes reflect the fact that the negative charge on the monobasic phosphonic acid moieties serves to raise the energy of the bpppH$^-$ $\pi$* and bpdpH$_2{}^{2-}$ $\pi$* levels and the MLCT transition becomes Ru(d$\pi$) $\rightarrow$ bpy($\pi$*) localized.

Luminescence spectra of $[(bpy)_2Ru(bpdpH_4)]^{2+}$ in 77 K matrixes of 4:1 ethanol/methanol having added acid or base are also observed to show pH dependence. Figure 3 shows emission spectra in acidic and basic glasses. The spectra illustrate that the average vibrational spacing and the relative excited state distortion (as estimated by the relative intensities of the 00 and 01 bands) are essentially the same for the protonated and deprotonated forms of the complex.

**D. Luminescence Quenching of Acid Complexes Metal Ion Following Complexation.** For ionic chromophores, ground state ion-pairing interactions can provide a means for efficient excited state quenching.[18] In such cases, quenching is observed at concentrations of the ionic quencher much lower than necessary for diffusion-limited bimolecular quenching. In addition, luminescence decays are double exponential in the presence of quencher, reflecting the decay of the chromophore with and without the ion-paired quencher. Previous studies of Ru(II) diimine complexes have shown that ion pairing with anionic transition metal complexes results in quenching of $[(bpy)_3Ru]^{2+}$ in aqueous solutions by both energy and electron transfer mechanisms.[19] The phosphonic acid containing complexes discussed here are different in that the ion-pairing interaction involves complexation with the phosphonic acid substituent and not the charged chromophore (a dicationic complex). In a relatively nonpolar mixed-solvent system, 4:1 CHCl$_3$/MeOH, quenching ions associate with the phosphonic acid residues at

(18) (a) Moggi, L.; Bolletta, F.; Maestri, M.; Balzani, V. *Proc. Int. Conf. Coord. Chem. 16th,* **1974**, 2.10a, 3p. (b) Bolletta, F.; Maestri, M.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1974**, *78*, 1374−1377. (c) Balzani, V.; Scandola, F. In *Photoinduced Electron Transfer. Part D: Inorganic Substrates and Applications*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; pp 148−178. (d) Balzani, V.; Sabbatini, N.; Scandola, F. *Chem. Rev.* **1986**, *86*, 319−337.

(19) (a) Balzani, V.; Ballardini, R.; Gandolfi, M. T.; Prodi, L. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Duerr, H., Eds.; VCH: Weinheim, Federal Republic of Germany, 1991; pp 371−391. (b) Ballardini, R.; Gandolfi, M. T.; Balzani, V. *Chem. Phys. Lett.* **1985**, *119*, 459−462.
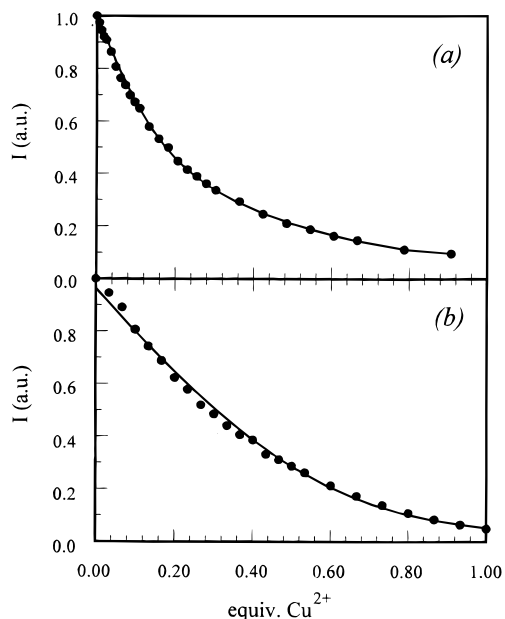
**Figure 5.** Relative integrated intensity of the emission as a function of the number of equivalents of $Fe^{3+}$ added for the (a) bpppH$_2$ and (b) bpdpH$_2$ complexes.

stoichiometric concentrations, even when the chromophore concentration is 1−10 $\mu$M. Efficient luminescence quenching of all three phosphonic acid complexes was observed with $Cu^{2+}$ and $Fe^{3+}$ in the CHCl$_3$/MeOH solution.

Luminescence spectra of $[(bpy)_2Ru(dpppH_2)]^{2+}$ in CHCl$_3$/MeOH in the presence of increasing amounts of $Fe^{3+}$ are shown in Figure 4; Figure 5 shows the relative integrated intensity of the emission as a function of the number of equivalents of $Fe^{3+}$ added for the dpppH$_2$ and bpdpH$_4$ complexes. The data illustrate that, for the bpppH$_2$ complex, more than half the MLCT emission is quenched following addition of only 0.1 equiv of $Fe^{3+}$ and the luminescence is essentially completely quenched in the presence of 0.5 equiv of $Fe^{3+}$. The implication is that the stoichiometry of the adduct between the $Fe^{3+}$ and the $[(bpy)_2Ru(dpppH_2)]^{2+}$ complex changes from approximately 5 $[(bpy)_2Ru(dpppH_2)]^{2+}$ per $Fe^{3+}$ to 2 of the Ru complexes per $Fe^{3+}$ as the concentration of $Fe^{3+}$ increases. For the bpdpH$_4$ complex the quenching results, shown in Figure 5, suggest a ratio of 2 $[(bpy)_2Ru(bpdpH_4)]^{2+}$ per $Fe^{3+}$ with complete quenching of the chromophore. The fact that no more than two phosphonic acid containing ligands can be bound to $Fe^{3+}$ for $[(bpy)_2Ru$-

**Figure 6.** Relative integrated intensity of the emission as a function of the number of equivalents of $Cu^{2+}$ added for the (a) bpppH$_2$ and (b) bpdpH$_2$ complexes.

(bpdpH$_4$)]$^{2+}$ is consistent with the fact that the $Fe^{3+}$ coordination environment will be more crowded with [(bpy)$_2$Ru(bpdpH$_4$)]$^{2+}$ as a "ligand" than with [(bpy)$_2$Ru(dpppH$_2$)]$^{2+}$.

Luminescence quenching was also observed with $Cu^{2+}$. Changes in the emission intensity with added $Cu^{2+}$ are shown in Figure 6 for both the bpdpH$_4$ and bpppH$_2$ complexes. The behavior of the bpdpH$_4$ complex with very little added $Cu^{2+}$ is similar to that for $Fe^{3+}$ quenching; a ratio of 2 [(bpy)$_2$Ru-(bpdpH$_4$)]$^{2+}$ complexes per $Cu^{2+}$ was observed. As the $Cu^{2+}$ concentration is increased, the 1:1 species begins to predominate, and nearly complete quenching is observed following the addition of 1 equiv of $Cu^{2+}$. Quenching of [(bpy)$_2$Ru(bpppH$_2$)]$^{2+}$ by $Cu^{2+}$ indicates 3:1 phosphonic acid/$Cu^{2+}$ complexes at low concentrations giving way to a 1:1 complex as the $Cu^{2+}$ concentration is increased (Figure 6).

The dynamics of the quenching reactions were studied by luminescence decay (time-correlated single photon counting) and transient absorption methods. For all the complexes in the presence of quenching metal ions luminescence decays are double exponential with a short component having a decay constant comparable to the lamp profile (1.5 ns) and a long component with a lifetime nearly the same as that of the unquenched complex. Thus, the observed steady state luminescence arises almost exclusively from the Ru(II) phosphonate complex not associated with the quenching metal ion. Rate constants for the rapid quenching process were obtained by ps transient absorption spectroscopy. Transients obtained for quenching of all three of the phosphonic acid complexes by both ions show only bleaching of the ground state MLCT absorbance of the Ru(II) complex in the 400−500 nm range. Each decay consists of a rapid recovery of the initial bleach and a long-lived species (>4 ns). Lifetimes of the short-lived transients are given in Table 4. Rate constants for the quenching of each complex can be calculated from the difference in excited state decay rate constants in the presence and absence of the quenching ions ($k_q = 1/\tau_q - 1/\tau_0$); values are reported in Table 4.

Luminescence data for the complexes in the absence and presence of quenching ions in ethanol/methanol glasses at 77

**Table 4.** Luminescence Lifetimes or Lifetimes Obtained by Transient Absorbance of Each Complex in the Presence of $Cu^{2+}$ and $Fe^{3+}$ Both in Solution at Room Temperature[a] and in 4:1 Ethanol/Methanol Glasses at 77 K

| complex | quenching ion | $\tau$, ns, 298 K | $k_q$, s$^{-1}$, 298 K | $\tau$, ns, 77 K | $k_q$, s$^{-1}$, 77 K |
|---|---|---|---|---|---|
| [(bpy)$_2$Ru(bpdpH$_4$)]$^{2+}$ | none | 400 | | 5006 | |
| | $Cu^{2+}$ | 0.14 | $7 \times 10^9$ | 14 | $7 \times 10^7$ |
| | $Fe^{3+}$ | <0.01 | $>1 \times 10^{11}$ | 21 | $5 \times 10^7$ |
| [(bpy)$_2$Ru(bpppH$_2$)]$^{2+}$ | none | 200 | | 5700 | |
| | $Cu^{2+}$ | 0.12 | $8 \times 10^9$ | 72 | $1 \times 10^7$ |
| | $Fe^{3+}$ | 0.09 | $1 \times 10^{10}$ | 109 | $9 \times 10^6$ |
| [(bpy)$_2$Ru(bpbzpH$_2$)]$^{2+}$ | none | 200 | | 4900 | |
| | $Cu^{2+}$ | 0.55 | $2 \times 10^9$ | | |
| | $Fe^{3+}$ | 0.38 | $3 \times 10^9$ | 425 | $2 \times 10^6$ |

[a] Solution quenching in undegassed 4:1 THF/MeOH.

K is also given in Table 4. Some luminescence quenching is observed for each ion for all the complexes, but both rate constants for the quenching process and the fraction of excited states quenched are smaller in the frozen matrix.

The above quenching, luminescence decay, and transient absorbance data do not clearly indicate the mechanism of the quenching process. Reaction of the MLCT state of the Ru(II) diimine complex with both $Fe^{3+}$ and $Cu^{2+}$ can occur by either electron transfer or exchange energy transfer. It is not possible to predict the free energies of the respective reactions because the coordination environment of the phosphonic acid bound metal ion quenchers is not known; however, estimates can be made using available redox potentials and spectroscopic data. For most $Cu^{2+}$ compounds in aqueous solution the Cu(II/I) potential is at positive potentials relative to SCE, making oxidation of the excited Ru(II) complex an exoergic process (eq 4).[20] Energy transfer is also possible with $Cu^{2+}$ since ligand

$$Ru^{II}* - PO_3Cu^{II} \rightarrow Ru^{III} - PO_3Cu^{I} \qquad (4)$$
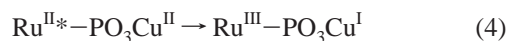
field states are lower in energy than the $^3$MLCT state of the Ru(II) complex and the energy transfer process is spin allowed (to populate the $^2T_{2g}$ state).[21] Both energy and electron transfer are also allowed for the ground state complex with Fe(III) bound to the phosphonate moiety; excited state electron transfer is exoergic for reduction of the Fe(III).

The available evidence suggests that, while electron transfer quenching cannot be discounted, exchange energy transfer occurs for all the complexes. This is based upon the observation that the luminescence is efficiently quenched even in glasses at low temperature (Table 4). Excited state electron transfer processes should be very slow in frozen solutions because the medium reorganizational energy for the process will be much larger than in fluid solution. Nonetheless, definitive evidence for exchange energy transfer was not obtained and electron transfer cannot be excluded.

Rate constants for quenching of the bpdpH$_4$ and bpppH$_2$ complexes are at least a factor of 3 faster than comparable rate constants for the bpbzpH$_2$ complex that has a methylene group between the chromophore and the phosphonic acid. In addition, rate constants in solution at room temperature are a factor of 100−1000 faster than values in low-temperature glasses. Since

(20) The excited state potentials of the Ru(II) phosphonate complexes can be estimated from the Ru(III/II) potentials and the excited state energy (Tables 1 and 2). Using the 77 K emission maxima as an estimate of the zero−zero emission energy, the Ru(III/II*) potentials are estimated to be +0.8 ± 0.1 V.

(21) See: Figgis, B. N. *Introduction to Ligand Fields*; Interscience Publishers: New York, 1966; Chapter 9.
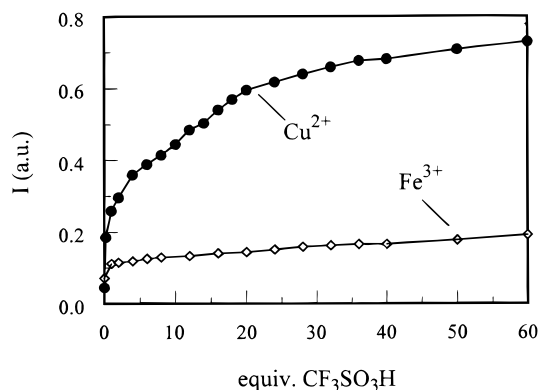
**Figure 7.** Recovery of luminescence upon addition of $CF_3SO_3H_2$ to solutions containing $[(bpy)_2Ru(bpppH_2)]^{2+}$ (40 $\mu$M) and 1 equiv of either $Fe^{3+}$ or $Cu^{2+}$.



**Figure 8.** Recovery of luminescence intensity upon addition of metal ions to a solution containing equal concentrations (40 $\mu$M) of $[(bpy)_2Ru(bpppH_2)]^{2+}$ and $Cu^{2+}$.

the coordination environment of the quenching ion cannot be determined, detailed discussion of the reaction dynamics is not possible.

**E. Effects of Added Acid and Cations on Quenching by $Fe^{3+}$ and $Cu^{2+}$.** Figures 5 and 6 indicate that $Cu^{2+}$ and $Fe^{3+}$ bind strongly to the phosphonate moieties of the three luminescent complexes. Association equilibrium constants for the two metals with the bpdpH$_4$ and the bpppH$_2$ complexes can be approximated using restricted models in which only particular coordination numbers are allowed. For association of $Fe^{3+}$ with $[(bpy)_2Ru(bpppH_2)]^{2+}$ (Ru) the data of Figure 5 were fit assuming that only Fe(Ru)$_6$, Fe(Ru)$_3$, and Fe(Ru)$_2$ complexes are present in significant concentration. The solid line of Figure 5a represents the fit assuming that the equilibrium constants for the Fe(Ru)$_6$, Fe(Ru)$_3$, and Fe(Ru)$_2$ complexes are $1.2 \times 10^{32}$ M$^{-6}$, $2.7 \times 10^{18}$ M$^{-3}$, and $1.6 \times 10^{13}$ M$^{-2}$, respectively. Association with $Cu^{2+}$ was fit to a model in which Cu(Ru)$_4$, Cu(Ru)$_2$, and Cu(Ru) are assumed to be the only significant species in solution. The best fit to the data assumes that the equilibrium constants for formation of the Cu(Ru)$_4$, Cu(Ru)$_2$, and Cu(Ru) complexes are $4.2 \times 10^{19}$ M$^{-4}$, $2.7 \times 10^{10}$ M$^{-2}$ and $6.5 \times 10^5$ M$^{-1}$, respectively. The data indicate that the $Fe^{3+}$ complexes are somewhat more stable than the $Cu^{2+}$ complexes. This is supported by the fact that the $Cu^{2+}$ is more readily dissociated upon addition of $CF_3SO_3H$ than is $Fe^{3+}$. Figure 7 illustrates the recovery of luminescence upon addition of the acid to solutions containing 1 eqiuv of $[(bpy)_2Ru(bpppH_2)]^{2+}$ and 1 equiv of either $Fe^{3+}$ or $Cu^{2+}$. Nearly complete displacement of $Cu^{2+}$ is observed following the addition of 30 equiv of acid, while no more than 20% of the original Ru complex luminescence has recovered following the addition of 60 equiv of acid to the $Fe^{3+}$ complex.

The phosphonate-bound $Cu^{2+}$ is also displaced by divalent metal ions that do not quench the luminescence of the Ru(II) complex. Figure 8 shows the effect on the MLCT luminescence intensity as a function of added metal ions to a solution containing equal concentrations of $[(bpy)_2Ru(dpppH_2)]^{2+}$ and $Cu^{2+}$. Group IIa and IIb ions readily displace $Cu^{2+}$. In addition, $Pb^{2+}$ was found to displace $Cu^{2+}$ to some extent; approximately 20% of the bound $Cu^{2+}$ was substituted by $Pb^{2+}$ in solutions containing equimolar amounts of the Ru(II) complex, $Cu^{2+}$ and $Pb^{2+}$. The fact that luminescence can be turned on by a trans-metalation reaction might provide an approach for the development of luminescence sensors for particular metal ions in other systems having higher selectivity.
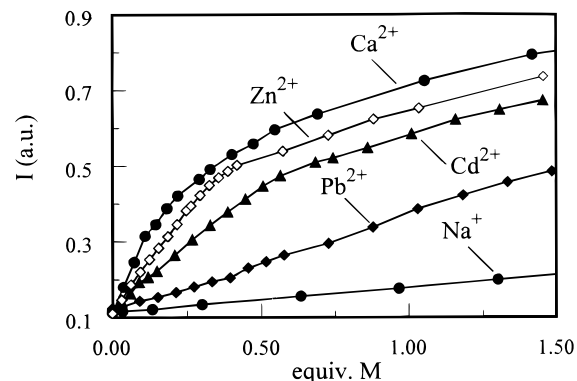
## Summary

The photophysical behavior of Ru(II) diimine complexes having ligands with diethyl phosphonate and phosphonic acid substituents was examined. The behavior resembled that of bipyridine carboxylate complexes in that the one-electron reduction of the ester complex occurs at more positive potentials than the one-electron reduction of the acid complex. Emission from the complex of bpdpH$_4$ is strongly pH dependent. The luminescence in strongly acidic solution originates from the Ru-$(d\pi) \rightarrow$ bpdpH$_4$ ($\pi$*) MLCT state; raising the pH results in a blue shift in the emission maximum and, based upon the relative ground and excited state p$K$ values, a change in the nature of the emissive excited state to Ru(d$\pi$) $\rightarrow$ bpy ($\pi$*) MLCT. The phosphonic acid complexes form ground state complexes with and are readily quenched by $Cu^{2+}$ and $Fe^{3+}$ in aprotic solvents.

## Experimental Section

**A. Syntheses.** All reactions were carried out in aerated solutions unless otherwise specified. 4,4′-Dibromo-2,2′-bipyridine,[22] 4-(*p*-methylphenyl)-2,2′-bipyridine,[23] and $[(bpy)_2RuCl_2]$[24] were prepared by literature methods. All solvents used were reagent grade and used without further purification unless otherwise noted.

**4-(Chloromethylphenyl)-2,2′-bipyridine.** A solution of 4-(*p*-methylphenyl)-2,2′-bipyridine (1.6 g, 6.4 mmol), *N*-bromosuccinimide (1.2 g, 6.5 mmol), and a small amount of dibenzoyl peroxide in CCl$_4$ (20 mL) was irradiated with a 150 W Xe arc lamp under N$_2$ for 4 h. The resulting solution was allowed to cool to room temperature, filtered to remove succinimide, and evaporated to dryness. The residue was dissolved in CHCl$_3$ and passed through a short column of alumina (neutral). The combined fractions from the column were evaporated to dryness to yield 1.4 g (75%). The product was checked for purity by gc−mass spectrometry (M$^+$: 280; 282) and was used without further purification.

**Diethyl [4-(2,2′-Bipyrid-4yl)benzyl]phosphonate, bpbzp.** 4-(Chloromethylphenyl)-2,2′-bipyridine (2.7 g, 9.6 mmol) was dissolved in triethyl phosphite (7 mL), and the mixture was refluxed for 50 min under a N$_2$ blanket. The solution was cooled to room temperature and chromatographed on neutral alumina using CHCl$_3$ as eluent. The combined bipyridine-containing fractions were evaporated to yield a pale yellow oil of the product (1.4 g, 38%). $^1$H NMR (CDCl$_3$): $\delta$ 8.34 (3H, m), 8.12 (1H, d), 7.44 (1H, t), 7.34 (2H, d), 7.13 (1H, d of d), 7.07 (2H, d), 6.94 (1H, t), 3.71 (4H, q), 2.85 (2H, d), 0.94 (6H, t).

**4-(*p*-Bromophenyl)-2,2′-bipyridine.** The ligand was made in three steps starting with 4-bromobenzaldehyde. To a rapidly stirred solution

(22) (a) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745. (b) Wenkert, D.; Woodward, R. B. *J. Org. Chem.* **1983**, *48*, 285−289.
(23) Li, Y. M.S. Thesis, Tulane University, New Orleans, LA, 1993.
(24) Sprintschnik, G. H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.

of 4-bromobenzaldehyde (9.73 g, 0.053 mol) in ethanol (200 mL) was added sodium pyruvate (6.36 g, 0.058 mol) dissolved in water (50 mL). The mixture was immersed in an ice bath, and 10% KOH (100 mL) was added slowly, the temperature being maintained between 5 and 10 °C. The mixture was stirred for 1.5 h; during this time the solution became bright yellow. The solution was then acidified to pH 6 with HCl and allowed to stand for 30 min as precipitate formed. The precipitate was filtered off, washed with cold water, and dried, yielding 4-bromo-(3-carboxyl-3-oxoprop-1-enyl)benzene (9.4 g, 0.04 mol, 75%). The product was used without further purification.

The 4-bromo-(3-carboxyl-3-oxoprop-1-enyl)benzene (8.8 g, 0.037 mol), 2-acetylpyridine pyridinium $PF_6$ (12.7 g, 0.037 mol), and ammonium acetate (22 g, 0.286 mol) were added to water (250 mL) and refluxed for 6 h. The precipitate formed was collected by filtration, washed with acetone, and dried overnight to yield 4-bromophenyl-6-carboxy-2,2′-bipyridine (11.1 g, 0.031 mol). The solid was sublimed under vacuum (190−210° C) and the sublimate collected to yield 4-(*p*-bromophenyl)-2,2′-bipyridine (6.14 g, 0.019 mol). ^{1}H NMR (acetone-$d_6$): δ 8.73 (1H, s), 8.71 (1H, d), 8.69 (1H, d), 8.50 (1H, d), 7.93 (1H, d of t), 7.79 (2 H, d), 7.72 (2H, d), 7.69 (1H, d of d), 7.43 (1H, d of t).

**Diethyl 4-(2,2′-Bipyrid-4-yl)phenylphosphonate, bppp.** The ligand was prepared by a method similar to that used by Hirao et al.[25] 4-(*p*-Bromophenyl)-2,2′-bipyridine (2.46 g, 0.008 mol) dried in vacuo at 35 °C overnight was added to an oven-dried 25 mL round-bottomed flask (rbf). An argon purge was placed on the rbf while triethyl phosphite (1.215 g, 0.0089 mol), triethylamine (1.220 g, 0.012 mol), and 5 mL of dry toluene were added. The mixture was stirred under an argon blanket until the bipyridine was dissolved. With a high argon purge, tetrakis(triphenylphosphine)palladium(0) (0.46 g, 0.0004 mol) was added. The dark brown solution was stirred at 90 °C under an argon blanket for 18 h. The completion of the reaction was monitored via TLC with 4:4:1 toluene/heptane/triethylamine as the eluent. After the addition of anhydrous diethyl ether (60 mL), triethylamine hydrobromide formed as a precipitate. The precipitate was removed by filtration and mother liquor dried by rotary evaporation. Flash column chromatography using a 4:4:1 toluene/heptane/triethylamine solution gave the resulting 4-(2,2′-bipyrid-4-yl)-phenylphosphonate as a viscous liquid. Dissolving in diethyl ether and allowing the solvent to evaporate overnight gave fine crystals (1.5328 g, 52.7%). ^{1}H NMR (CD₃CN): δ 8.76 (1H, d), 8.74 (1H, d), 8.49 (1H, d), 7.90 (5 H, m), 7.73 (1H, d of d), 7.42 (1H, d of t), 4.11 (4 H, m), 1.29 (6 H, t).

**4,4′-(Diethyl phosphonato)-2,2′-bipyridine, bpdp.** 4,4′-Dibromo-2,2′-bipyridine (0.94 g, 3 mmol) was dissolved in anhydrous toluene (10 mL) and stirred under nitrogen for 20 min. Diethyl phosphite (1.12 g, 8.2 mmol) and triethylamine (0.84 g) were added with a syringe, and the mixture was stirred for an additional 10 min; finally with a high nitrogen purge tetrakis(triphenylphosphine)palladium was added and the mixture heated at 80−90 °C for 3 h. The reaction was monitored via TLC with 4:4:1 toluene/heptane/triethylamine as the eluent. After cooling to room temperature diethyl ether was added to the reaction mixture to precipitate the triethylamine hydrobromide, which was removed by filtration. The filtrate was evaporated to give a yellow oil. The crude product was purified by column chromatography on silica gel with 4:4:1 toluene/heptane/triethylamine eluent to yield 0.8 g (63%) of product. ^{1}H NMR (CDCl₃): δ (ppm) 1.35 (t, 12H), 4.18 (m, 8H), 7.72 (ddd, 2H), 8.76 (d, 2H), 8.83 (t, 2H). ^{31}P NMR (CDCl₃): δ (ppm) 15.68. Elemental Anal. Calcd (found) for $C_{18}H_{26}O_6P_2N_2$: C, 50.45 (49.87); H, 6.12 (6.14); N, 6.54 (6.32).

(25) Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 909−913.

**4,4′-Bis(phosphonato)-2,2′-bipyridine, bpdpH₄.** Acetonitrile was first distilled from calcium hydride and then dried with activated molecular sieves. Dichloromethane was dried with activated molecular sieves. 4,4′-Bis(diethylphosphonate), 2,2′-bipyridine (0.3 g, 70.1 mmol), and 1:1 acetonitrile/dichloromethane (25 mL) were added to a 50 mL rbf, and the solution was degassed with argon. Bromotrimethylsilane (1.2 mL, 8.92 mmol) was added via syringe, and the reaction mixture was refluxed under an atmosphere of argon overnight. A white precipitate was observed in the reaction mixture on refluxing overnight. After cooling to room temperature, water was added dropwise with stirring to the reaction mixture until a white precipitate formed. The solid was filtered and dried in vacuo to yield a white powder (0.2 g, 90.3%). ^{1}H NMR (D₂O): δ (ppm) 7.64 (ddd, 2H), 8.58 (d, 2H), 8.76 (t).

**Ru[(bpy)₂(bpbzp)](PF₆)₂.** A mixture of Ru(bpy)₂Cl₂ (0.452 g, 1.3 mmol), diethyl [4-(2,2′-bipyrid-4yl)benzyl]phosphonate (0.428 g, 1.1 mmol), and 1:1 ethanol/water (50 mL) was stirred and refluxed under an atmosphere of argon for 2 h. The orange-red solution was allowed to cool to room temperature and was reduced to half volume via rotary evaporation. The product was precipitated by adding excess NH₄PF₆ to the solution and cooling at 0 °C overnight. The product was collected by filtration, dried in a vacuum oven overnight at 30 °C, and chromatographed on neutral alumina using CH₃CN/toluene (2:1). The orange column fraction was evaporated to dryness, taken up in a minimum of CH₃CN, and precipitated by addition to a rapidly stirred solution of diethyl ether. Yield: 0.56 g (55%). Elemental anal. Calcd (found) for $C_{41}H_{39}N_6O_3P_3F_{12}Ru \cdot H_2O$: C, 44.60 (44.24); H, 3.74 (3.74); N, 7.61 (7.58).

**Ru[(bpy)₂(bpdp)](PF₆)₂.** A mixture of Ru(bpy)₂Cl₂ (0.060 g, 0.124 mmol), 2,2′-bipyridine-4,4′-bis (diethylphosphonate) (0.080 g, 0.186 mmol), and 1:1 ethanol/water (50 mL) was stirred and refluxed under an atmosphere of argon for 6 h. The orange-red solution was allowed to cool to room temperature and was reduced to half volume via rotary evaporation. The solution was cooled in the refrigerator for 30 min, and the product was precipitated by adding excess NH₄PF₆ to the solution and cooling at 0 °C overnight. The product was filtered through a fritted funnel and dried in a vacuum oven overnight at 30 °C. Yield: 0.079 g (56%). Elemental anal. Calcd (found) for $C_{38}H_{42}O_6P_4 N_6F_{12}$-Ru: C, 40.32 (38.80); H, 3.71 (3.64); N, 7.43 (6.94).

**[(bpy)₂Ru(4-(2,2′-bipyrid-4-yl)phenylphosphonate)](PF₆)₂, [(bpy)₂Ru-(dppp)](PF₆)₂.** Ru(bpy)₂Cl₂ (0.5951 g, 0.0011 mol) and 4-(2,2′-bipyrid-4-yl)phenylphosphonate (0.4986 g, 0.0014 mol) were dissolved in 40 mL of a 1:1 ethanol/water mixture in a 100 mL rbf. After the solution was refluxed for 4 h under Ar purge, the purple color disappeared to yield a deep red solution. The solution was placed on a rotary evaporator until most of the ethanol was removed. Saturated aqueous NH₄PF₆ was added dropwise, resulting in precipitation of a red solid. The sample was filtered, washed with 20 mL of water three times, and dried in vacuo overnight to yield [(bpy)₂Ru(4-(2,2′-bipyrid-4-yl)phenylphos-phonate)](PF₆)₂ (1.10 g, 92.4%). Elemental anal. for $C_{40}H_{37}N_6O_3P_3F_{12}$-Ru: found (calcd): C, 44.08 (44.83); H, 3.50 (3.48); N, 7.64 (7.84).

**[(bpy)₂Ru(4-(2,2′-bipyrid-4-yl)phenylphosphonic acid)](PF₆)₂ [(bpy)₂Ru(bpppH₂)](PF₆)₂.** Care must be taken in the preparation of the glassware. After the reaction flask (25 mL rbf) was dried in an oven at 180 °C overnight, the flask was then washed with 5% chlorotrimethylsilane. The glassware was then dried further at 35 °C in a vacuum oven for 3 h. Acetonitrile was first distilled from calcium hydride and then dried further using molecular sieves. Dichloromethane was dried using molecular sieves. [(bpy)₂Ru(dppp)](PF₆)₂ (0.500 g, 0.00047 mol) was added to the 25 mL rbf, and an argon blanket was applied. Twenty-five milliliters of 50:50 acetonitrile/dichloromethane solution was added to dissolve the complex. Bromotrimethylsilane (0.40 mL, 0.0035 mol) was added dropwise by syringe, and the rbf was sealed. The solution was stirred for 24 h at room temperature and then refluxed for an additional 4 h under Ar. To the flask was added 10 mL of water dropwise to hydrolyze the silane complex. An additional 25 mL of water was added in preparation for rotary evaporation. Acetonitrile and dichloromethane were removed by rotary evaporation to leave a deep red aqueous solution. NH₄PF₆ was added to precipitate the metal complex. The red precipitate was filtered and washed with 25 mL of water and 25 mL of ethanol. The filtrate was vacuum-dried and

reprecipitated in ether to yield [(bpy)$_2$Ru(4-(2,2′-bipyrid-4-yl)phe-nylphosphonic acid)](PF$_6$)$_2$ (0.320, 67.5%).

**Ru[(bpy)$_2$(bpbzpH$_2$)](PF$_6$)$_2$.** The procedure is the same as that used for [(bpy)$_2$Ru(bpppH$_2$)](PF$_6$)$_2$. Yield: 0.149 g (78%).

**Electrochemical Measurements.** Redox potentials for the phosphonate ester complexes were measured by both cyclic voltammetry and differential pulse polarography in CH$_3$CN with a glassy carbon working electrode and SSCE reference unless otherwise noted. Ferrocene was added as an internal reference.

**Luminescence Measurements.** Luminescence spectra of the diethyl phosphonate complexes were obtained in room temperature acetonitrile and ethanol/methanol (4:1) glasses at 77 K. Spectra were obtained using a SPEX fluorimeter with a CCD detector; spectra were not corrected for detector response. Luminescence quantum yields of the diethyl phosphonate complexes in acetonitrile and the phosphonic acid complexes in water were measured at room temperature using [(bpy)$_3$Ru](PF$_6$)$_2$ in H$_2$O[26] as reference.

**Luminescence Decay Rate Measurements.** Luminescence lifetimes were measured by time-correlated single photon counting using a home-built system described elsewhere.[27] In all cases reported here decays were fit as either single or double exponentials using a modified Marquardt algorithm.

**Picosecond Absorption Measurements.** Transient decays were measured using a regeneratively amplified Ti:sapphire laser for both pump and probe pulses. The absorption experiment has been described previously.[28] Decays were measured using 2 mm path length absorbance cells with excitation of the MLCT absorption at 400 nm. In typical experiments a 5−10-fold stoichiometric excess of the quenching ion was used.

(26) Van Houten, J.; Watts, R. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(27) Taffarel, E.; Chirayil, S.; Kim, W. Y.; Thummel, R. P.; Schmehl, R. H. *Inorg. Chem.* **1996**, *35*, 2127.

(28) Kipp, R. A.; Li, Y.; Simon, J. A.; Schmehl, R. H. *J. Photochem. Photobiol. A*. **1999**, *121*, 27.