Inorg. Chem. **2002**, *41*, 6688–6694

Inorganic Chemistry
Article

Synthesis and Photochemistry of Ru(II) Complexes Containing Phenanthroline-Based Ligands with Fused Pyrrole Rings

John M. Villegas, Stanislav R. Stoyanov, and D. P. Rillema*

*Department of Chemistry, Wichita State University, 1845 N Fairmount,
Wichita, Kansas 67260-0051*

Received July 3, 2002

Hydrolysis of 1,10-phenanthrolinopyrrole ethyl ester leads to the acid derivative which is unstable at room-temperature releasing CO_2 and forming 1,10-phenanthrolinopyrrole (php). The ligand reacts with ruthenium(II) to form a series of complexes of the general formula $[Ru(php)_n(bpy)_{3-n}]^{2+}$, where bpy = 2,2′-bipyridine and $n = 1$–3. The photochemical properties reveal that the complexes have longer-lived excited states than the standard complex, $[Ru(bpy)_3]^{2+}$. Their emission lifetimes range from 9.04 μs ($n = 1$) to 35.5 μs ($n = 3$) at 77 K compared to 7.57 μs for the standard. Similarly, at room-temperature, emission lifetimes range from 1.20 μs ($n = 1$) to 1.70 μs ($n = 3$) relative to the standard (0.56 μs). The emission quantum yields also have higher values than the standard $[Ru(bpy)_3]^{2+}$ under similar conditions. The temperature-dependent studies for the complexes establish the distribution among the radiative, nonradiative, and ^{3}MLCT to ^{3}d–d decay channels and are in agreement with the energy gap law.

Introduction

There is currently considerable interest on the part of scientists to find alternative sources of energy for fossil fuels. This is triggered by the fact that growing environmental concerns arise from the use of fossil fuels, which aggravates the greenhouse effect by releasing CO_2 in combustion,[1] and the concern about the depletion of fossil fuel reserves. The sun possesses our greatest source of renewable energy. Plants take advantage of its potential as an energy source in the photosynthesis process by converting sunlight into stored energy. Plants utilize solar energy to approximately 10 times our current energy needs.[2,3]

The idea of harnessing solar energy[4] for practical usage has led to the development of the Grätzel cell which utilizes dyes attached to a TiO_2 electrode.[5] When these dyes absorb light, an electron is initially transferred from the metal to a ligand, then to the TiO_2 acceptor,[6,7] and finally to the cathode where I_3^- is reduced to I^-. The produced I^- then reduces the dye back to its original oxidation state. These cells are about 12% efficient but have a potential efficiency of ~28%. Therefore, the search continues to find dyes capable of reaching this peak efficiency value.

$[Ru(bpy)_3]^{2+}$ is the most well-known and thoroughly studied photosensitizer.[8] Derivatives of this complex have been extensively examined for their chemical stability, redox[9,10] and magnetic[11,12] properties, excited-state reactivity,[13] and emission and lifetime characteristics.[8,14−17]

---

* To whom correspondence should be addressed. E-mail: paul.rillema@wichita.edu.

(1) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Simon and Schuster: Heme Hempstead, England; 1990, pp 1−28.
(2) Campell, M. K. *Biochemistry* 2nd ed.; Saunders College Publishing: Philadelphia, 1995.
(3) Wayne, P. R. *Principles and applications of Photochemistry*; Oxford University Press: New York, 1988.
(4) Kutal, C. *J. Chem. Educ.* **1983**, *60*, 882.
(5) Balzani, V.; Bolletta, F.; Ciano, M.; Maestri, M. *J. Chem. Educ.* **1983**, 447.
(6) Murakishi, K.; Kano, G.; Wada, Y.; Yanaguda, S.; Miyazaki, H.; Matsumoto, M.; Murasawa, S. *J. Electoanal. Chem.* **1995**, *396*, 27−34.
(7) Nasr, C.; Kamat, P.; Hotchandani, S. *J. Phys. Chem. B* **1998**, *102*, 10047−10056.
(8) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(9) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.
(10) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.
(11) Jimenez-Aparicio, R.; Urbanos, F. A.; Arrieta, J. M. *Inorg. Chem.* **2001**, *40*, 613.
(12) Miyasaka, H.; Clerac, R.; Campos-Fernandez, C. S.; Dunbar, K. R. *Inorg. Chem.* **2001**, *40*, 1663.
(13) D'Angelantonio, M.; Mulazzani, Q. G.; Venturi, M.; Ciano, M.; Hoffman, M. Z. *J. Phys. Chem.* **1991**, *95*, 5121−9.
(14) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.
(15) Watts, R. *J. Chem. Educ.* **1983**, *60*, 834.
(16) Klassen, D. M.; Crosby, G. A. *J. Chem. Phys.* **1965**, *43*, 1498.

10.1021/ic020436a CCC: $22.00

Ru(II) diimine complexes containing carboxylate,[18,19] sulfonate,[20] catechol,[21] and phosphonate[22] "anchor" groups for absorption on nanostructured TiO_2 surfaces have been prepared and their properties investigated. Information on the energy level matching between the dyes and TiO_2 has been obtained through electron spectroscopy.[23]

Other related studies that have recently appeared follow. The energy transfer rate in crystals of double complex Ru(II)−Cr(III) salts was found to be strongly dependent on the relative orientation between the complexes.[24] Ru(II) complexes that involved cyclodextrins as luminescent receptors have been developed in aqueous solution. Photoinduced electron transfer occurred from the Ru(II) center to the Os(III) metalloguest even though the two metal moieties were not covalently bound.[25] A molecular assembly based on zeolites was prepared using $[Ru(bpy)_2(bpz)]^{2+}$, $[Ru(bpy)_2(H_2O)_2]^{2+}$ as a sensitizer/donor diad and MV^{2+} (methyl viologen) as an acceptor.[26] Ru(II)-polypyridine-based assemblies that incorporate supramolecular, noncovalently connected moieties and covalently linked systems were proposed as energy storage systems.[27,28] Decanuclear dendrimeric antennas that incorporate Ru(II), Os(II), and Pt(II) were reported, and photophysical studies revealed that all the absorbed energy was channeled to the central Os-based unit.[29]

For a complex to be considered an effective light absorption sensitizer, certain criteria have to be met.[30,31] The complex must absorb energy typically from the UV to the near-IR region of the spectrum. It must be stable to thermal and photochemical decomposition and must have a long-lived excited state and a high photochemical quantum yield.[4]

Here, we report the synthesis of a series of Ru(II) diimine dyes that are potentially good sensitizers with longer lifetimes and higher quantum yields than most other Ru(II) polypyridine complexes. The change in their emission properties with temperature was determined in order to deduce the luminescence decay pathways and to learn whether emission lifetimes followed the energy gap law.

Experimental Section

Materials. The precursor 5-nitro-1,10-phenanthroline was purchased from GFS Chemicals. Ethyl isocyanoacetate, NH_4PF_6, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from Aldrich. Tetrahydrofuran, 2-propanol, and methanol were optima grade and purchased from Fisher Scientific. Ruthenium trichloride trihydrate was obtained from Pressure Chemical Company. The synthesis of *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) and tetrachloro(2,2′-bipyridine)ruthenium(IV) were prepared according to published procedures.[32,33] Absolute ethanol was purchased from AAPER Alcohol and Chemical Company. Ethanol and methanol were used in a 4:1 (v/v) mixture to prepare the solutions for the absorption, emission, and emission lifetime studies. Elemental analyses were obtained from M-W-H Laboratories, Phoenix, AZ.

(1) 1,10-Phenanthrolinopyrrole Ethyl Ester (php-COOEt).[34] A 2.24 g sample of 5-nitro-1,10-phenanthroline (10 mmol) was dissolved in 120 mL of a 1:1 2-propanol/THF mixture in a 250 mL round-bottom flask. The solution was stirred for 10−15 min. Then, 1.08 mL of ethyl isocyanoacetate (10 mmol) was added into the solution followed by 3 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) producing a brownish-yellow solution. The stirring was continued overnight. A yellow precipitate formed and was removed by filtration. It was then washed with 10 mL of ether (3×) and 10 mL of water (3×) and dried in a vacuum oven (yield: 60%). Anal. Calcd for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.42. Found: C, 69.96; H, 4.62; N, 14.39. IR (KBr pellet): 3091, 2977, 1687, 1560, 1376, 1284, 1171, 1124, 1049, 739 cm^{-1}. ^1H NMR (DMSO): δ ppm 1.42 (t, 3H, $J = 6.8$ Hz, CH_3), 4.43 (q, 2H, $J = 7.2$ Hz, CH_2), 7.69 (m, 2H, CH), 8.39 (s, 1H, CH), 8.81 (dd, 1H, $J = 1.6$, 8.0 Hz, CH), 8.88 (dd, 1H, $J = 1.6$, 4.4 Hz, CH), 8.94 (dd, 1H, $J = 1.6$, 4.4 Hz, CH), 10.07 (dd, 1H, $J = 2.0$, 8.2 Hz, CH), 13.08 (1H, NH).

(2) 1,10-Phenanthrolinopyrrole (php). A 1.53 g sample of php-COOEt (5.3 mmol) was added to 80 mL of 1:1 ethanol/0.2 M NaOH in a 125 mL round-bottom flask. The solution was refluxed for 6−8 h after which the stirring was continued at room-temperature for another 30−60 min. The tan precipitate was filtered and washed with ether. The solid was recrystallized in methanol and dried in a vacuum oven (yield: 90%). Anal. Calcd for $C_{14}H_9N_3$ (containing 0.5 mol of methanol): C, 74.03; H, 4.71; N, 17.86. Found: C, 73.16; H, 4.68; N, 17.38. IR (KBr pellet): 3094, 1597, 1578, 1553, 1424, 1402, 1382, 1086, 802, 781, 678, 609 cm^{-1}. ^1H NMR (DMSO): δ ppm 7.57 (m, 2H, CH), 7.94 (s, 2H, CH), 8.56 (dd, 2H, $J = 1.6$, 4.8 Hz), 8.76 (dd, 2H, $J = 1.4$, 8.2 Hz), 12.13 (1H, NH).

(3) $[Ru(bpy)_2(php)](PF_6)_2$. A sample of $Ru(bpy)_2Cl_2$ (0.25 mmol) was mixed with php (0.25 mmol) in a 250 mL round-bottom flask. About 100 mL of absolute ethanol was added, and the solution was refluxed for 4−5 h. It was then filtered to remove unreacted reagents. The solution was diluted with water to about 200 mL, and saturated NH_4PF_6 was added to precipitate an orange complex. The complex was filtered and washed with ether (3 × 15 mL). It was then dried in a vacuum oven. The complex was dissolved in methanol and reprecipitated in ether (yield: 98%). Anal. Calcd for

---

(17) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 23.

(18) Gholamkhass, B.; Koike, K.; Negishi, N.; Hori, H.; Takeuchi, K. *Inorg. Chem.* **2001**, *40*, 576.

(19) Shan, B.-Z.; Zhao, Q.; Goswami, N.; Eichhorn, D. M.; Rillema, D. P. *Coord. Chem. Rev.* **2001**, *211*, 117−144.

(20) Schwarz, O.; van Loyen, D.; Jockusch, S.; Turro, N. J.; Durr, H. *J. Photochem. Photobiol., A* **2000**, *132*, 91−98.

(21) Rice, C. R.; Ward, M. D.; Nazeeruddin, M. K.; Grätzel, M. *New J. Chem.* **2000**, *24*, 651−652.

(22) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Pechy, P.; Rotzinger, F. P.; Humphry-Baker, R.; Kalyanasundaram, K.; Grätzel, M.; Shklover, V.; Haibach, T. *Inorg. Chem.* **1997**, *36*, 5937−5946.

(23) Rensmo, H.; Westermark, K.; Sodergren, S.; Kohle, O.; Persson, P.; Lunell, S.; Siegbahn, H. *J. Chem. Phys.* **1999**, *111*, 2744−2750.

(24) Otsuka, T.; Sekine, A.; Fujigasaki, N.; Ohashi, Y.; Kaizu, Y. *Inorg. Chem.* **2001**, *40*, 3406.

(25) Haider, J. M.; Chavarot, M.; Weidner, S.; Sadler, I.; Williams, R. M.; De Cola, L.; Pikramenou, Z. *Inorg. Chem.* **2001**, *40*, 3912.

(26) Bhuiyan, A. A.; Kincaid, J. *Inorg. Chem.* **2001**, *40*, 4464.

(27) Heinz, D.; Bossman, S.; Heppe, G.; Schwarz, R.; Thiery, U.; Trierweiler, H. P. *Proc.−Indian. Acad. Sci., Chem. Sci.* **1993**, *105*, 435−450.

(28) David, E.; Van Loyen, D.; Born, R.; Bossman, S.; Duerr, H.; Willner, I. *J. Inf. Rec.* **1998**, *24*, 277−284.

(29) Sommovigo, M.; Denti, G.; Serroni, S.; Campagna, S.; Mingazzini, C.; Mariotti, C.; Juris, A. *Inorg. Chem.* **2001**, *40*, 3318.

(30) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; von Zelewski, A. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 78.

(31) Balzani, V.; Juris, A.; Scandola, F. In *Homogeneous and Heterogeneous Photocatalysis;* Pelizzetti E., Serpone, N., Eds.; Reidel: Dordrecht, The Netherlands, p 1, 1986.

(32) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(33) Krause, R. A. *Inorg. Chem. Acta* **1977**, *22*, 209−213.

(34) Lash, T. D.; Novak, B. H.; Lin, Y. *Tetrahedron Lett.* **1994**, *35*, 2493−4.

$RuC_{34}H_{25}N_7P_2F_{12}$: C, 44.26; H, 2.73; N, 10.63. Found: C, 44.11; H, 2.74; N, 10.57. IR (KBr pellet): 3405, 1602, 1559, 1522, 1466, 1446, 1412, 1243, 1161, 1099, 840, 759, 730, 557 cm^{-1}. MS: $m/z = 316$ amu for $[Ru(bpy)_2(php)]^{2+}$. ^1H NMR (DMSO): δ ppm 7.42 (dd, 2H, $J = 6.4, 7.2$ Hz), 7.56 (dd, 2H, $J = 5.6, 7.6$ Hz), 7.69 (m, 6H), 7.82 (d, 2H, $J = 4.8$ Hz), 8.13 (dd, 2H, $J = 7.2, 8.0$ Hz), 8.19 (dd, 2H, $J = 7.6, 8.0$ Hz), 8.24 (s, 2H), 8.79 (dd, 2H, $J = 1.6, 7.6$ Hz), 8.85 (t, 4H, $J = 8.4$ Hz), 12.68 (1H, NH).

(4) $[Ru(bpy)(php)_2](PF_6)_2$. A sample of php (0.1714 g, 0.78 mmol) was placed in a 100 mL round-bottom flask and mixed with $Ru(bpy)Cl_4$ (0.0857 g, 0.21 mmol). About 15 mL of ethylene glycol was added, and the solution was refluxed for 2−3 h. After cooling the solution, it was filtered to remove unreacted reagents. The solution was diluted with water to 75 mL and saturated with NH_4PF_6 resulting in the formation of a reddish-brown precipitate. The complex was filtered, washed with ether (3 × 15 mL), and dried in a vacuum oven. It was dissolved in methanol and recrystallized in ether. (Yield: 63%). Anal. Calcd. for $RuC_{38}H_{26}N_8P_2F_{12}$: C, 46.31; H, 2.66; N, 11.37. Found: C, 46.12; H, 2.76; N, 11.09. IR (KBr pellet): 3422, 1600, 1584, 1558, 1519, 1437, 1410, 1094, 841, 726, 558 cm^{-1}. MS: $m/z = 348$ amu for $[Ru(bpy)(php)_2]^{2+}$. ^1H NMR (DMSO): δ ppm 7.46 (dd, 2H, $J = 6.4, 7.2$ Hz), 7.60 (dd, 2H, $J = 3.0, 5.1$ Hz), 7.71 (dd, 2H, $J = 2.7, 6.0$ Hz), 7.78 (dd, 2H, $J = 1.4, 5.1$ Hz), 7.98 (dd, 2H, $J = 3.3, 8.1$ Hz), 8.16 (t, 2H, $J = 8.1$ Hz), 8.20 (s, 2H), 8.24 (s, 2H), 8.76 (dd, 2H, $J = 1.2, 7.2$ Hz), 8.85 (dd, 2H, $J = 1.2, 6.6$ Hz), 8.89 (dd, 2H, $J = 1.2, 4.8$ Hz), 9.01 (d, 2H, $J = 6.9$ Hz), 12.68 (2H, NH).

(5) $[Ru(php)_3](PF_6)_2$. A sample of $RuCl_3{\cdot}3H_2O$ (0.0461 g, 0.176 mmol) in a 100 mL round-bottom flask was added to an excess of php (0.2268 g, 1.04 mmol). About 15 mL of ethylene glycol was added, and the solution was refluxed for 2−3 h. After cooling, it was filtered to remove unreacted reagents. The solution was diluted with water to 75 mL and saturated with NH_4PF_6 resulting in the formation of a dark brown precipitate. The complex was filtered, washed with ether (3 × 15 mL), and dried in a vacuum oven. It was dissolved in methanol and reprecipitated in ether (yield: 60%). Anal. Calcd for $RuC_{42}H_{27}N_9P_2F_{12}$: C, 48.10; H, 2.59; N, 10.02. Found: C, 48.30; H, 2.62; N, 10.19. IR (KBr pellet): 3408, 1599, 1518, 1439, 1095, 841, 557 cm^{-1}. MS: $m/z = 379$ amu for $[Ru(php)_2]^{2+}$. ^1H NMR (DMSO): δ ppm 7.61 (q, 6H, $J = 8.1$ Hz), 7.76 (dd, 6H, $J = 1.4, 5.2$ Hz), 8.24 (s, 6H), 8.77 (dd, 6H, $J = 1.2, 8.1$ Hz), 12.68 (3H, NH).

Physical Measurements. UV−vis spectra were obtained using a Hewlett-Packard model 8452A diode array spectrophotometer. The IR spectra were obtained using a Perkin-Elmer model 1600 FT-IR spectrophotometer. Proton NMR spectra were obtained using Varian Mercury 300 and Varian Inova 400 FT-NMR spectrometers. ESI-MS spectra were collected using a Finnigan LCQ-Deca ion-trap mass spectrometer (Thermoquest, San Jose, CA). An EG&G PAR model 263A potentiostat/galvanostat was used to obtain the cyclic voltammograms. The measurements were carried out in a typical H-cell using a platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode in CH_3CN. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAH). Ferrocene was added as a reference compound.

The corrected emission spectra were obtained using a Spex Fluorolog 212 spectrofluorometer. The emission quantum yields were determined using $[Ru(bpy)_3]^{2+}$ as the standard having a known emission quantum yield of 0.089 ± 10% at 25 °C in 4:1 ethanol/methanol.[35] All emission samples were prepared in HPLC grade or better solvents, filtered through 0.45 μ PTFE filters, and then freeze−pump−thaw degassed a minimum of three times prior to the measurements.

The sample preparation for photophysical measurements involved dissolving a small amount of sample (∼2 mg) in the appropriate solvent, and the absorbance of the solution was measured. The concentration of the solution was altered in order to achieve an absorbance of about 0.10 at 450 nm. Such a concentration provides enough material for data acquisition but excludes self-quenching processes. A 3−4 mL aliquot of the solution was then placed in a 10 mm diameter Suprasil (Heraeus) nonfluorescent quartz tube equipped with a tip-off manifold. The sample was then freeze−pump−thaw degassed for at least three cycles (to approximately 75 millitorr) removing any gases from the sample. The manifold was then closed, and the sample was allowed to equilibrate at room temperature. The solvent evaporation was assumed to be negligible; therefore, the concentrations were assumed to remain constant throughout this procedure. The emission quantum yields were then calculated using eq 1, where ϕ_x is the emission quantum yield of the sample, ϕ_{std} is the emission quantum yield for the standard, A_{std} and A_x represent the absorbance of the standard and the sample, respectively, while I_{std} and I_x are the integrals of the emission envelope of the standard and the sample, respectively.[19]

$$\phi_x = (A_{std}/A_x)(I_x/I_{std})\phi_{std} \tag{1}$$

The excited-state lifetimes were determined by exciting the sample at 450 nm using an OPOTEK optical parametric oscillator pumped by a frequency tripled Continuum Surlite Nd:YAG laser run at ∼20 mJ/10 ns pulse. The oscilloscope control and data curve fitting analysis were accomplished with a program developed in-house. The temperature-dependent decay data fits were made with Microcal Origin Version 3.5 by Microcal Software, Inc.

Results

Synthesis. The synthesis of **2** was carried out according to the scheme presented in Figure 1A. When **1** was treated with 0.2 M NaOH, it produced phpCOOH which was isolated and characterized. The latter was thermally unstable and underwent decarboxylation forming **2**. In the presence of a strong base and ethanol, however, **1** could be directly converted to **2**. The same process occurred when **1** was complexed first with the $[Ru(bpy)_2]^{2+}$ moiety, followed by hydrolysis to form **3**. The kinetics and mechanism of the decarboxylation of a similar system have been reported.[36]

Syntheses of Ru(II) heterocyclic complexes starting with Ru(IV), Ru(III), and Ru(II) precursors have often been carried out in reducing solvents such as ethanol. To provide enough thermal energy for the reaction to proceed and still maintain a reducing environment, the preparation of **4** and **5** using Ru(IV) and Ru(III), respectively, was carried out in ethylene glycol because of its high boiling point.[37] On the other hand, **3** was prepared by directly reacting **2** with $Ru(bpy)_2Cl_2$ in ethanol. Figure 1B shows schematically the preparation of the complexes. The compounds were characterized using IR, ^1H NMR, and elemental analysis.

---

(35) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thompson, A. J.; Glasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293.

(36) Dunn, G. E.; Lee, G. K. *Can. J. Chem.* **1971**, *49*, 1032−35.

(37) Blanton, C. B. M.S. Thesis, The University of North Carolina at Charlotte, NC, 1990 and references therein.

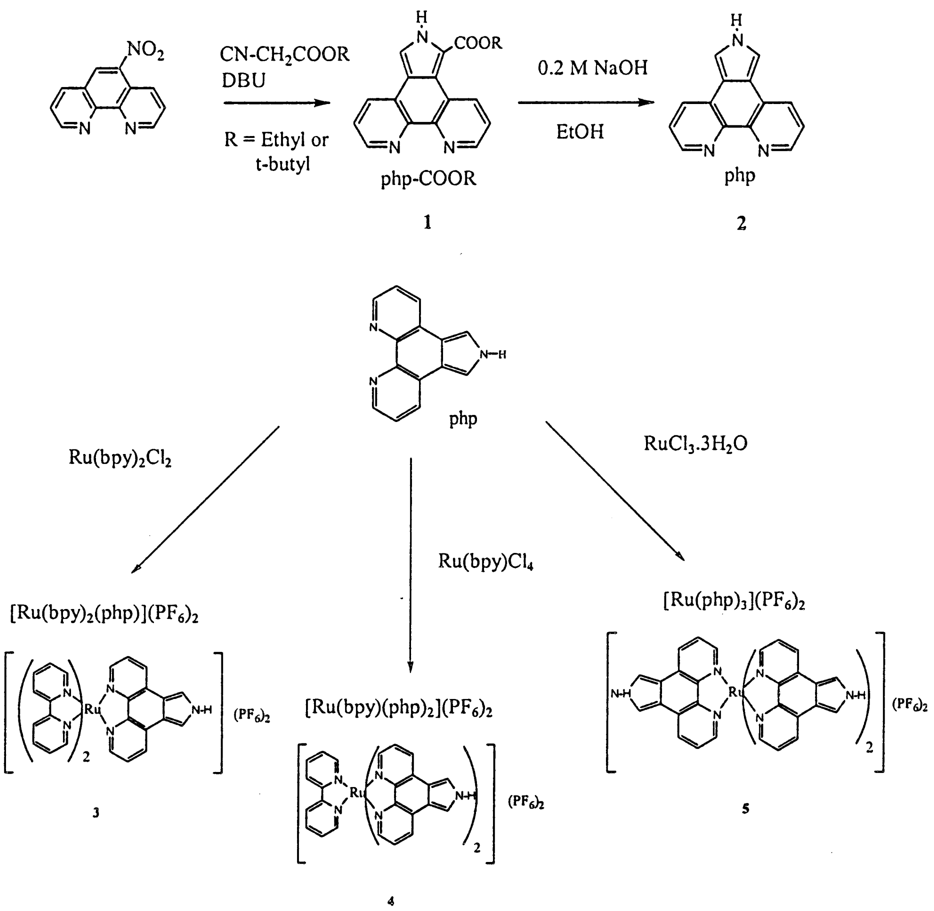

Figure 1. (A) Synthesis of the ligand. (B) Synthesis of the complexes.

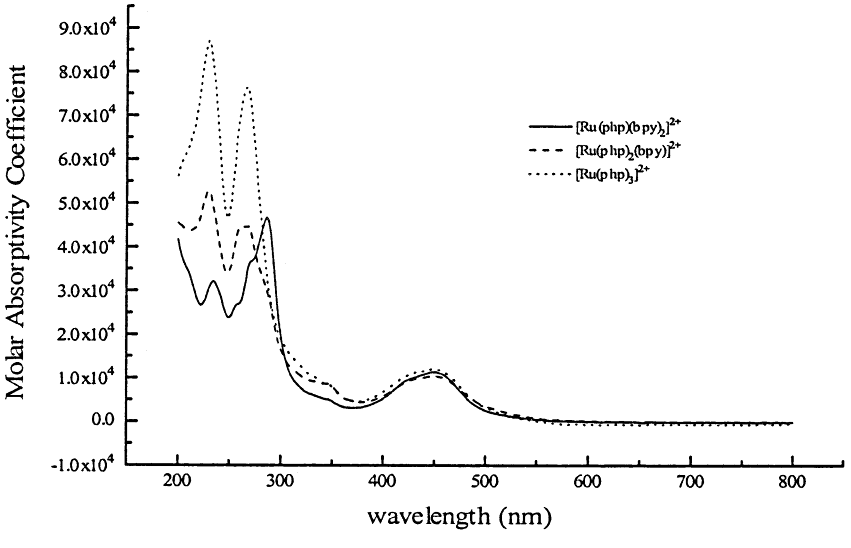

Figure 2. UV spectra of the Ru(II) complexes.

Electronic Studies. The electronic properties were determined using a UV–vis spectrophotometer at room temperature with ethanol/methanol (4:1) as solvent. The results of the studies are listed in Table 1. The absorption coefficients were obtained from Beer's Law studies and determined from at least five dilution points. The complexes showed typical metal-to-ligand charge transfer (MLCT) transitions consistent with Ru(II) polypyridyl systems as presented in Figure 2.[8] Two distinct sets of absorption bands were present for all three complexes under investigation. The probable assignment of these bands was made on the basis of the well-documented optical transitions in $[Ru(bpy)_3]^{2+}$.[38–40]

Electrochemical Studies. The electrochemical properties of the complexes were summarized in Table 2. An irreversible oxidation for $[Ru(bpy)_2(php)]^{2+}$ was observed at 1.37

---

(38) Rillema, D. P.; Taghdiri, D. G.; Jones, D. S.; Keller, C. D.; Worl, L. A.; Meyer, T. J.; Levy, H. A. *Inorg. Chem.* **1987**, *26*, 578.

(39) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849.

Table 1. Electronic Transitions of Ru(II) Complexes in EtOH/MeOH (4:1) at Room Temperature

complex	MLCT ($d\pi \rightarrow \pi^*$), λ (nm), ϵ (M^{-1} cm^{-1})	LC ($\pi \rightarrow \pi^*$), λ (nm), ϵ (M^{-1} cm^{-1})
$[Ru(bpy)_2(php)]^{2+}$	450 (15 230)	286 (60 740), 234 (41 560)
$[Ru(php)_2(bpy)]^{2+}$	450 (10 660)	268 (44 880), 230 (53 060)
$[Ru(php)_3]^{2+}$	450 (12 120)	266 (75 310), 230 (85 840), 286 (118 046)
$[Ru(bpy)_3]^{2+}$	450 (16 371)	254 (84 936), 244 (88 673)

Table 2. Electrochemical Properties of the Complexes in Acetonitrile[a]

complex	$E_{1/2}$, V[b]	$E_{1/2}$, V (L)$^{0/-1/-2/-3}$ [b]
$[Ru(bpy)_2(php)]^{2+}$	1.37 (irr)[c]	−1.35 −1.60
$[Ru(php)_2(bpy)]^{2+}$	1.40 (irr)[c]	−1.89
$[Ru(php)_3]^{2+}$	1.40 (irr)[c]	
$[Ru(bpy)_3]^{2+}$	1.27[d]	−1.31 −1.50 −1.77

[a] Room Temperature, 0.10 M TBAH, scan rate = 250 mV/s. [b] Potential in volts vs SSCE. [c] Oxidation wave was irreversible. [d] $Ru^{III/II}$ redox couple.

V and shifted slightly to a more positive potential (1.40 V) as the number of coordinated php ligands increased. The reduction peaks of the coordinated 2,2′-bipyridine ligands shifted to more negative potentials as the number of php ligands increased. No reduction of the coordinated php ligand was observed for the complexes; its reduction apparently was outside the electrochemical window of the solvent used. The observations remained the same using different solvents, electrolytes, working electrodes, and scan rates.

Excitation and Emission Properties and Quantum Yields. The excitation and emission studies were carried out at both 77 and 298 K. The properties of the three complexes were within the range characteristic for Ru(II) diimine systems.[8,41] At 298 K (Figure 3A), only one broad and less structured emission peak was observed similar to those reported for $[Ru(bpy)_3]^{2+}$.[42,43] This was resolved into two structured peaks at 77 K (Figure 3B) where the major emission peak shifted to a higher energy at 571−577 nm and the second peak resulting from vibronic coupling with the ring breathing mode[44] was located in the 615−622 nm range for the three complexes of the series. The red shift of the emission maxima as the temperature increased from 77 K to room-temperature is consistent with the MLCT nature of the process. The solvent obviously plays an important role in responding to the photoinduced dipole change thereby facilitating the relaxation to the ground state in the room-temperature measurements.

The emission quantum yields of the series of complexes were determined relative to the standard, $[Ru(bpy)_3]^{2+}$, at room temperature in the same solvent mixture. The complexes exhibited decreasing quantum yields from **3** to **5**, but all had higher emission quantum yields than the standard. The results are tabulated in Table 3.

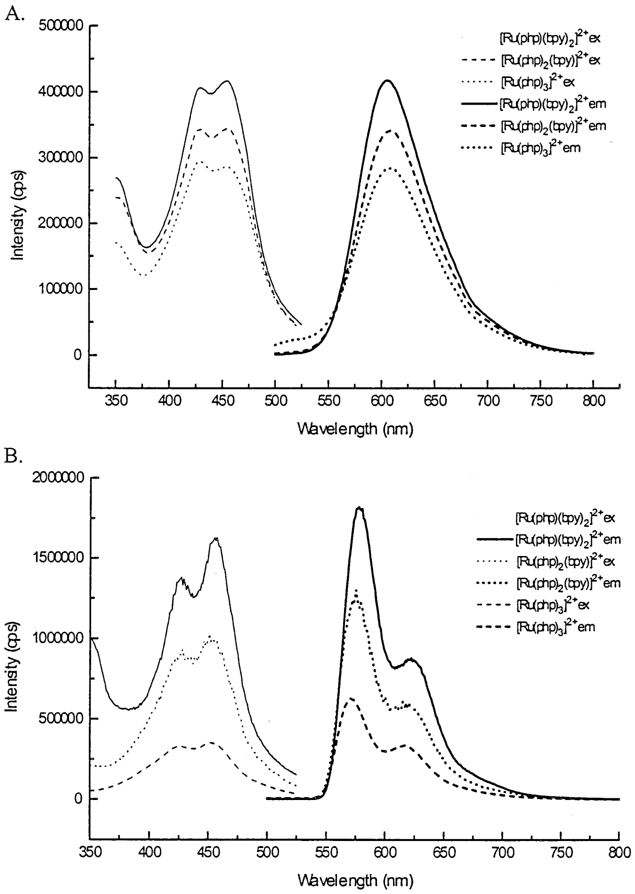

Figure 3. Excitation and emission spectra of the complexes at (A) 298 K and at (B) 77 K.

Excited-State Lifetimes and Kinetic Studies. Emission lifetime studies were carried out at both 77 and 298 K with 4:1 ethanol/methanol as solvent (Table 4). The emission lifetimes of **3**−**5** increased from about 1.2 μs to about 1.7 μs. It is worthy to note that the lifetimes of these complexes are much longer than that for the standard $[Ru(bpy)_3]^{2+}$ at both temperatures.

The temperature dependence of the emission lifetimes was measured in 5 K increments over the 220−295 K temperature range using an average of 300 sweeps per measurement. The temperature dependence followed the relation in eq 2 given by Van Houten and Watts.[42−46] A single-exponential fit of the emission decay versus temperature was performed

$$1/\tau(T) = k_0 + k_1 e^{-\Delta E/k_B T} \tag{2}$$

using eq 2, and the results are presented in Figure 4. The values of k_0, k_1, and ΔE as well as the standard deviations are listed in Table 4. The results obtained were in the range of those reported previously for Ru(II) polypyridyl complexes.[47,48]

Discussion

Excited-State Decay Rate Constants (k_0). The study of the emission decay at varied temperature can be used to

---

(40) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 2589.

(41) Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanton, C. B.; White, R. P. *Inorg. Chem.* **1989**, *28*, 1013.

(42) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031−37.

(43) Hager, G. D.; Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7037−42.

(44) Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: Orlando, FL, 1992; p 124.

(45) Van Houten, J. C.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853−58.

(46) Van Houten, J. C.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381−85.

Table 3. Emission Properties and Lifetimes of the Ru(II) Complexes in 4:1 EtOH/MeOH at 77 K and RT (298 K)

complex	λ_{ex}, (nm) 77 K	λ_{ex}, (nm) 298 K	λ_{em}, (nm) 77 K	λ_{em}, (nm) 298 K	ϕ_{em}, 298 K	τ, (ns) 77K	τ, (ns) 298K
$[Ru(bpy)_2(php)]^{2+}$	427, 455	429, 453	577, 622	606	0.123	9041.59	1234.79
$[Ru(php)_2(bpy)]^{2+}$	428, 451	429, 455	575, 615	608	0.099	11667.80	1622.85
$[Ru(php)_3]^{2+}$	427, 452	429, 454	571, 617	608	0.095	35461.00	1704.74
$[Ru(bpy)_3]^{2+}$	426, 455	427, 454	576, 622	600	0.089	7567.16	555.56

Table 4. Kinetic Parameters for the Emission Decay of the Ru(II) Complexes in 4:1 EtOH/MeOH

complex	k_{nr}, (s^{-1}) × 10^5	k_r, (s^{-1}) × 10^4	k_0, (s^{-1}) × 10^5	k_1, (s^{-1}) × 10^{11}	ΔE, (cm^{-1})
$[Ru(bpy)_2(php)]^{2+}$	4.08 ± 0.03	9.96 ± 0.03	5.08 ± 0.03	4.6 ± 3.4	4288 ± 227
$[Ru(php)_2(bpy)]^{2+}$	3.15 ± 0.02	6.10 ± 0.02	3.76 ± 0.02	27 ± 1.3	4759 ± 152
$[Ru(php)_3]^{2+}$	3.50 ± 0.05	5.57 ± 0.05	4.06 ± 0.05	62 ± 59	4872 ± 290
$[Ru(bpy)_3]^{2+(53)}$	5.20 ± 0.5	8.0 ± 1.5	6.10 ± 0.05	40 ± 20	3275 ± 75

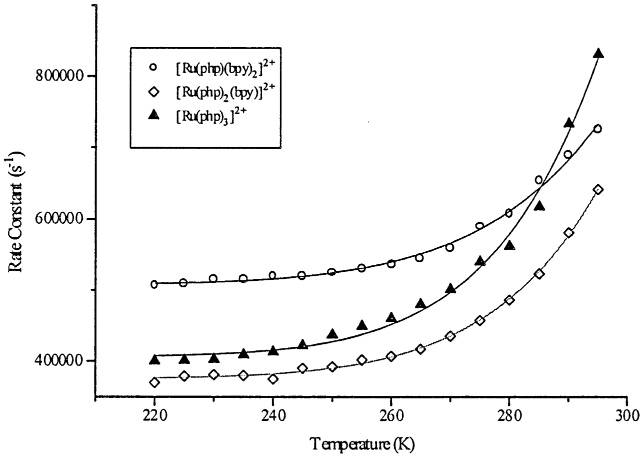

Figure 4. Temperature dependence of the luminescence lifetime for the Ru(II) complexes in 4:1 EtOH/MeOH.

determine the partitioning of energy among the three decay channels: radiative, nonradiative, and ^{3}MLCT → ^{3}d−d. The temperature-dependent term of eq 2 has been interpreted as involving thermal population of the near-lying ^{3}d−d state from the emitting ^{3}MLCT excited state.[42−46,49] The energy gap between these two states, ΔE (Table 4), increases slightly from **3** to **5** and is higher than that for $Ru(bpy)_3^{2+}$. The rate constant for the process (k_1) increases with the number of php ligands in the complex. The temperature dependence of the decay time, τ, is due to the activated surface crossing of the electron from the ^{3}MLCT to the ^{3}d−d state following the general model for the photophysics of Ru(II) polypyridyl complexes.[49−57] The excited-state species then undergoes photochemical and/or thermal energy loss.[52,57,58]

The rate constant, k_0 in eq 2, includes both radiative, k_r, and nonradiative, k_{nr}, contributions to the rate of the ^{3}MLCT excited-state decay. Assuming that the temperature dependences of k_r and k_{nr} are negligible,[50] the values of k_r and k_{nr} can be determined using data from emission quantum yield

$$k_0 = k_r + k_{nr} \tag{3}$$

(ϕ_{em}) studies and eq 4, where T is the temperature and η_{isc} is the efficiency of population of the emitting ^{3}MLCT states following excitation. At room temperature, η_{isc} for Ru(II)

$$\phi_{em}(T) = \eta_{isc} k_r \tau(T) \tag{4}$$

complexes in liquid solution is generally assumed to be unity.[59−63] Thus, eqs 3 and 4, using values of τ and ϕ_{em}, both estimated at 25 °C, were used to determine the values of k_r and k_{nr}.[47] The k_r values calculated from emission lifetimes and emission quantum yields for the series (eq 4) gave values that were in the range expected for Ru(II) polypyridyl emitters.[48,64]

The emission lifetimes of the complexes remained nearly constant in the 220−250 K range and decreased rapidly thereafter. The lifetime studies, however, showed an increasing trend from **3** to **5**. The three complexes exhibited higher lifetimes than $[Ru(bpy)_3]^{2+}$ at both 77 and 295 K. The results are consistent with the energy gap law.

Radiative Decay Rate Constants (k_r). For a spontaneous emission, the radiative rate constant is related to the Einstein coefficient[65] as represented by eq 5, where E_{em} represents the energy at maximum emission intensity in ergs, ψ_e and

$$k_r = [4E_{em}{}^3/3\hbar^4]|<\psi_e|\vec{d}\psi_g>|^2 \tag{5}$$

ψ_g are the wave functions for the excited and the ground electronic states, and $\vec{d}$ is the transition dipole moment operator. It is evident from the data gathered that the ratio of $k_r/E_{em}{}^3$ is relatively constant within the luminophoric

---

(47) Laguitton-Pasquier, H.; Martre, A.; Deronzier, A. *J. Phys. Chem. B* **2001**, *105*, 4801−09.
(48) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613−20.
(49) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803−10.
(50) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967−77.
(51) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583−90.
(52) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277.
(53) Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1993**, *97*, 11956−59.
(54) Creutz, C.; Chow, M.; Netzel, M.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309−19.
(55) Morris, D. E.; Hanck, K. W.; De Armond, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 3032−38.
(56) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444−53.
(57) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyd, S.; Jones, W. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473−487.
(58) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193−1206.
(59) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697−2705.
(60) Klassen, D. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853−58.
(61) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177−79.
(62) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 1800−01.
(63) Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCuster, J. K. *Science* **1997**, *275*, 54−57.
(64) Treadway, J. A.; Loeb, B.; Lopez, R.; Anderson, P. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2242.
(65) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: New York, 1950; Vol 1.

series. The values of k_r ranged from 5.6×10^4 to 1.0×10^5 s^{-1} and are in agreement with the values for other series of $Ru(bpy)_nL_{3-n}^{2+}$ complexes, where $n = 1-3$.[48] This indicates that the transition dipole moments, $<\psi_e|\epsilon|\psi_g>$, are relatively small within the series and that k_r values for the Ru-based MLCT excited states are relatively unaffected by substitution of bpy by php as a luminophoric ligand.

Nonradiative Decay Rate Constants (k_{nr}). The energy gap law for nonradiative decay sets is $\ln(k_{nr}) \propto E_{em}$, but this relationship was not plotted for the complexes of the series because complexes **4** and **5** had the same emission energies at 298 K. However, at 77 K, as the emission energy increased from **3** to **5**, the $\ln(k_{nr})$ value for **3** was higher than those for **4** and **5**. According to the energy gap law, k_{nr} decreases as ΔE increases (Table 4). Hence, the influence of k_r increases in eq 3 resulting in an increase in τ as found in this study. The increase may be due to loss of the twisting motion about the bridgehead carbon atoms of the bpy ligand upon substitution of the php ligand for $[Ru(bpy)_2(php)]^{2+}$, but for $[Ru(bpy)(php)_2]^{2+}$ and $[Ru(php)_3]^{2+}$, where this same effect is expected, the decrease in k_r may be the result of a decrease in the intersystem crossing quantum yield from the singlet excited state to the triplet emitting state.

Electrochemical Behavior. The electrochemical behavior of the complexes was anomalous. The oxidation of the $Ru^{III/II}$ couple for most diimine ruthenium complexes is normally reversible and located in the 1.4−1.3 V region, and the reduction of coordinated 2,2′-bipyridine normally commences at ∼ −1.3 V and shifts negatively in a systematic manner allowing calculation of the thermodynamic energy gap which parallels that of the electronic emission energy. The irreversible oxidation for the complexes examined in this report occurred in the region where the $Ru^{III/II}$ couple normally is observed causing confusion about the assignment, but it may be due to irreversible oxidation of the php ligand, vide infra. Consequently, one cannot obtain values for the thermodynamic energy gap, ΔE, obtained from the difference between the first oxidation and first reduction for these complexes. Reductions with the exception of $[Ru(bpy)_2(php)]^{2+}$ are also unusual. First, the php ligand did not undergo reduction even though it is basically a 1,10-phenanthroline, and second, the $[Ru(php)_2(bpy)]^{2+}$ complex reduces at almost 0.3 V more negative a potential than expected. Thus, for these complexes, it is not possible to use the difference in potential between the first oxidation and reduction to support the observed electronic energy gap as has been done in the past. So, we have turned to theoretical calculations to augment our study.

Theoretical Calculations. Density functional theory (DFT) calculations of the three complexes were performed, and the B3LYP optimized geometries and electronic structures were produced using a 3-21G(*) basis set. Previously reported linear correlation coefficients, based on a series of 10 Ru(II) diimine complexes,[66] were used to calculate the expected MLCT band energies. The calculated band energies were found to correlate well with the lowest energy transitions observed for the complexes tabulated in Table 1. The calculated values were 459, 459, and 444 nm for $[Ru(bpy)_2(php)]^{2+}$, $[Ru(bpy)(php)_2]^{2+}$, $[Ru(php)_3]^{2+}$, respectively, compared to the experimentally observed value of 450 nm for each.

Further analysis of the results from DFT calculations for the three complexes revealed that the spatial distribution of the frontier orbitals differed from that of the standard, $[Ru(bpy)_3]^{2+}$. The HOMO for all the complexes in the series was on the metal center with a characteristic dz^2 shape similar to that of $[Ru(bpy)_3]^{2+}$. However, unlike $[Ru(bpy)_3]^{2+}$, HOMO − 1 and HOMO − 2 were almost degenerate ($\Delta E = 0.01$ eV) and were located on the php ligands. The difference between HOMO and HOMO − 1 was ca. 0.1 eV. Thus, the irreversible oxidations can be explained by an initial oxidation of Ru(II) to Ru(III) followed by the irreversible oxidation of php ligands resulting in the absence of the cathodic peak as discussed in the previous section.

The spatial distribution of LUMO + 1 and LUMO + 2 was similar to that of the LUMO for the series with the frontier orbitals located on the bpy ligand(s) for $[Ru(bpy)_2(php)]^{2+}$ and $[Ru(bpy)(php)_2]^{2+}$, but on the bpy moiety of the php ligand for $[Ru(php)_3]^{2+}$ similar to $[Ru(bpy)_3]^{2+}$. However, for LUMO + 3, the frontier orbitals extended onto the pyrrole, 0.9 eV higher in energy than the LUMO. Hence, communication between the pyrrole and bpy moieties of the php ligand did not occur; therefore, the excited-state properties seem unaffected by the presence of the pyrrole portion of the php ligand.

Conclusion

A series of Ru(II) complexes containing 1,10-phenanthroline with a fused pyrrole ring were synthesized and characterized. The complexes exhibited normal MLCT transitions as observed from the absorption spectra. The complexes showed Φ_{em} and τ values higher than those for the standard $[Ru(bpy)_3]^{2+}$ both at 77 K and at room temperature. The results for the radiative and nonradiative decay rate constants calculated from the exponential fit of the emission decay versus the temperature were in agreement with previous studies on Ru(II) diimine complexes. The radiative decay rate was not found to be strongly dependent on the substitution of 2,2′-bipyridines with php, and the nonradiative rate constant within the series $[Ru(bpy)_2(php)]^{2+}$, $[Ru(bpy)(php)_2]^{2+}$, and $[Ru(php)_3]^{2+}$ was in general agreement with the energy gap law at 77 K.

The complexes contain a potential second binding site for other metals at the pyrrole nitrogen. Work on the synthesis of binuclear complexes involving **2** and a php-based porphyrin is in progress.

Acknowledgment. We thank the Department of Energy, The National Science Foundation, Johnson Matthey, Inc., and the Office of Research Administration at WSU for support.

IC020436A

---

(66) Stoyanov, S. R.; Villegas, J. M.; Rillema, D. P. *Inorg. Chem.* **2002**, *41*, 2941.