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# 2,2′:4,4″:4′,4‴-Quaterpyridyl: A Building Block for the Preparation of Novel Redox Reagents. 2. Bis(2,2′-bipyridine)ruthenium(II) Complexes[1]

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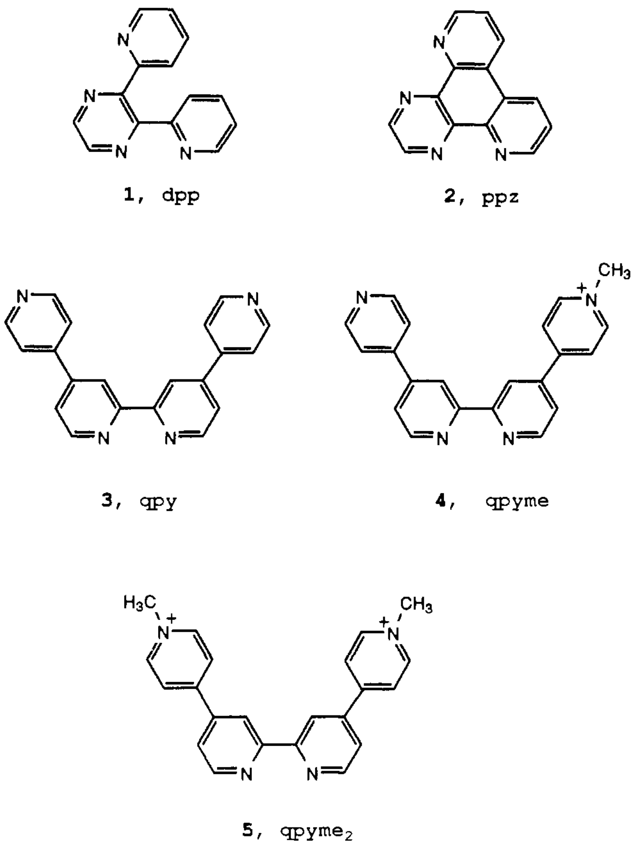
The syntheses and properties of three new ruthenium(II) complexes based on the ligand 2,2′:4,4″:4′,4‴-quaterpyridyl (qpy) are reported. Each new complex is of the type $[Ru(bpy)_2L]^{n+}$, where L is the parent qpy ligand or is qpy derivatized by the methylation of one or both of the non-$\alpha$-diimine nitrogen atoms and $n$ = 2,3, or 4. The photophysical and electrochemical properties of the new complex ions are reported. The parent ion $[Ru(bpy)_2qpy]^{2+}$ is strongly luminescent and has a relatively long lifetime, e.g. in excess of 1400 ns in acetonitrile solution. In contrast, the lifetime of the dimethyl derivative $[Ru(bpy)_2(qpyme_2)]^{4+}$ is less than 100 ns. This dimethylated complex has some novel properties. The excited state produced by M-L excitation to the $qpyme_2^{2+}$ ligand can be considered in terms of a Ru(III) core and a *positively* charged ligand. Typically, the excited states of other ruthenium(II) diimine complexes have had neutral or negatively charged ligands. Further, in structural terms, the complex can be considered as an intramolecular assembly of a ruthenium(II) diimine site and a viologen site. Cyclic voltammetry indicates that the first two electrons added to the complex enter the viologen-like acceptor site constituted by the $qpyme_2^{2+}$ ligand.

## Introduction

Ruthenium(II) polypyridine complexes have a unique combination of spectroscopic[2] and electrochemical[3] properties. The ion $[Ru(bpy)_3]^{2+}$ has a relatively long-lived excited state that is a potent oxidant and reductant. It has proven to be ideal for many fundamental studies of photophysical and photochemical electron-transfer[4] and energy-transfer[5] properties. Many other rubidium(II) polypyridine complexes share these properties, modified in various ways by the particular polypyridine or diamine ligand being used. Significant applications of ruthenium(II) bipyridine complexes as photocatalysts have been investigated. Among these are the photoinduced cleavage of water[6] and the photoreduction of carbon dioxide,[7] both major goals of research in the area of artificial photosynthesis.[8] In addition, some ruthenium polypyridine complexes have potential as components of electrochromic devices,[9] while others exhibit intercalative binding to DNA and show promise as site-specific probes for polynucleotides.[10]

Increasing importance is being attached to the rational design and synthesis of complexes with desired properties. "Fine-tuning" of advantageous properties has been achieved through the synthesis of a great many polypyridines and related ligands. A recent review lists many examples.[2] However, most such compounds cannot easily be modified either before or after complexation to a metal ion. Fine-tuning has generally required the de nouveau synthesis of completely new ligands and complexes. Ligands that afford opportunities for straightforward structural elaboration have obvious advantages. Our recent efforts have focused on the synthesis of diimine ligands of this type.[1,11] Earlier papers have described the properties of Ru(II) complexes containing the ligands **1** and **2** (Chart I).

**Chart I**



1, dpp

2, ppz

3, qpy

4, qpyme

5, qpyme$_2$

In the first paper of this series[1] we described the preparations of 2,2′:4,4″:4′,4‴-quaterpyridyl (**3**) and of its methylated derivatives **4** and **5**. All possess a diimine site for coordination to a

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metal, as well as other (non-diimine) nitrogen atoms that can be used for structural elaboration. Furthermore, complexation to ruthenium(II) of the N-methylated compounds **4** and **5** leads to compounds having a photoactive electron-donor site and a viologen-type electron-acceptor site in the same molecule. This is of potential interest, since one approach to circumvent the energy wasting back electron transfer step[12] in the use of ruthenium (II) polypyridine complexes in the conversion of solar energy is to organize the sensitizer and quencher into a single molecule.[8,13]

We have also become interested in the interactions of Ru(II) complexes with DNA. Complexes of ligands **3**–**5**, and analogues, are of interest in light of their structural similarity to 4,7-diphenyl-1,10-phenthroline, whose ruthenium(II) complex has been found to be a sensitive probe of DNA conformation.[14] In this paper, part 2 of the series, we report the ground-state and excited-state properties of the ruthenium(II) bis(2,2′-bipyridine) complexes of **3**–**5**. Work on the interaction of these complexes with DNA is described elsewhere.[15]

## Experimental Section

**Materials.** Nitrogen gas was dried by passage through a column of $P_2O_5$, followed by a column of $CaCl_2$. Acetonitrile was distilled over $P_2O_5$ prior to its use in electrochemical measurements. All other reagents were used as received from chemical suppliers without purification.

**Physical Measurements.** Cyclic voltammograms were recorded on a PAR 173 system as described in our earlier publications.[11] Millimolar samples were examined in acetonitrile solution with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte. The cell was purged for 10 min with nitrogen prior to the recording of voltammograms. The working electrode was a platinum disk, and the auxiliary, a platinum screen, and potentials were measured versus the standard calomel electrode (SCE). The resonance Raman spectrophotometer has been previously described.[16] Absorption spectra were recorded on a Cary 14 spectrophotometer. Emission spectra were recorded on a Perkin-Elmer Hitachi MPF-2A emission spectrophotometer equipped with a red-sensitive Hamamatsu R818 photomultiplier. Emission quantum yields, $\Phi_{em}$, were measured as previously described, using $[Ru(bpy)_3]^{2+}$ in water as the standard. Excited-state lifetimes were measured using a Quanta-Ray DCR-2A Nd:YAG laser with 355-nm excitation. The luminescence was analyzed at 90° to the direction of excitation by first passing the emitted light through a Bausch and Lomb 33-86-76 monochromator. An RCA 31034A photomultiplier was employed. The output of the photomultiplier was sent to a Tektronix 7834 oscilloscope, and photographs were taken of the oscilloscope trace. Lifetimes were calculated by the usual method of finding the time for the luminescence to decay to 1/*e* of its intensity at the time of the pulse.

Oxidative and reductive excited state potentials were calculated according to eq 1 and 2, respectively, where $A^+/A$ and $A/A^-$ are the

$$E(A^+/A^*) = E(A^+/A) - E^{0-0} \qquad (1)$$

$$E(A^*/A^-) = E(A/A^-) + E^{0-0} \qquad (2)$$

potentials for the first reduction and oxidation of the complex. $E^{0-0}$ was approximated as the maximum of the luminescence spectrum.

The radiative, $k_r$, and nonradiative, $k_{nr}$, rate constants were computed from the uncorrected emission spectra using eqs 3 and 4, which assume the efficiency of intersystem crossing to be unity.

$$k_r = \Phi_{em}/\tau \qquad (3)$$

$$k_{nr} = 1/\tau - k_r \qquad (4)$$

**Preparation of Bis(2,2′-bipyridine) Complexes of 3–5.** $Ru(bpy)_2Cl_2$ (100 mg) and 1 equiv of L (L = **3**–**5**) were refluxed in 100 mL of ethanol (50%) for 2 h. The deep red solution so obtained was filtered while hot, and the volume was reduced to 10 mL. This solution was added dropwise into 20 mL of a saturated aqueous solution of ammonium hexafluorophosphate. The salt which precipitated was collected by filtration and chromatographed on alumina (neutral, 80–200 mesh). The column was packed and developed with acetonitrile. The complexes were eluted by adding increasing amounts of methanol to the mobile phase. Fractions were collected and their emission spectra recorded. The fractions which exhibited a maximum, listed in Table III, consistent with the desired complex were combined, the solvent was removed under reduced pressure (60 °C), and the solid collected.

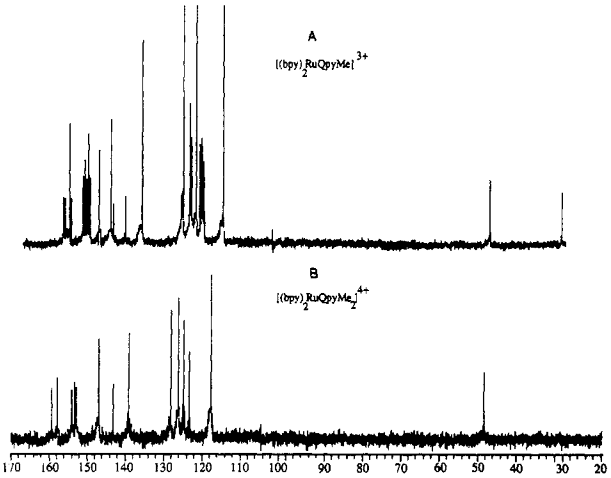

**Figure 1.** $^{13}C$ spectra of (A) $[Ru(bpy)_2qpyme]^{3+}$ and (B) $[Ru(bpy)_2(qpyme_2)]^{4+}$ as their $PF_6^-$ salts in $CD_3CN$. (The peaks at 120 ppm in both spectra are due to solvent.)

**Table I.** $^{13}C$ NMR Resonances ($\delta$)[a]

| no. | $[Ru(bpy)_2qpyme]^{3+}$ | $[Ru(bpy)_2(qpyme_2)]^{4+}$ |
|---|---|---|
| 1 | 49.6 | 49.6 |
| 2 | 124.0 | |
| 3 | 124.2 | |
| 4 | 124.3 | |
| 5 | 124.4 | |
| 6 | 125.8 | 125.9 |
| 7 | 127.0 | 127.3 |
| 8 | 127.3 | 127.3 |
| 9 | 129.2 | 129.2 |
| 10 | 139.6 | 139.8 |
| 11 | 143.7 | 143.8 |
| 12 | 146.8 | 147.5 |
| 13 | 150.4 | |
| 14 | 152.7 | |
| 15 | 152.8 | 152.7 |
| 16 | 153.0 | |
| 17 | 153.2 | 153.3 |
| 18 | 153.8 | 154.4 |
| 19 | 158.1 | |
| 20 | 158.2 | 158.0 |
| 21 | 158.8 | 158.2 |
| 22 | 159.7 | 159.4 |

[a] Saturated solutions in $CD_3CN$. Values measured relative to TMS.

C, H, N analyses are as follows. Found for $[Ru(bpy)_2qpy]^{2+}(PF_6^-)_2$: C, 47.89; H, 3.16; N, 11.20. Calc: C, 47.39; H, 2.97; N, 11.01. Found for $[Ru(bpy)_2qpyme]^{3+}(PF_6^-)\cdot 5H_2O$: C, 39.29; H, 2.79; N, 8,89. Calc: C, 39.02; H, 3.12; N, 8.89. Found for $[Ru(bpy)_2(qpyme_2)]^{4+}(PF_6^-)_4$: C, 37.34; H, 2.74; N, 8.32. Calc: C, 37.34; H, 2.52; N, 8.50.

## Results

**Synthesis and Characterization.** The bis(pyridine) complexes of the parent quaterpyridyl, $[Ru(bpy)_2L]^{2+}$ (L = 3–5), can be prepared in satisfactory yield by refluxing $Ru(bpy)_2Cl_2$ with 1 equiv of the respective ligand in 50% ethanol. Characterization of complexes containing ligands **3**–**5** was accomplished using NMR spectroscopy and elemental microanalysis. Particularly important in confirming that the methyl groups on ligands **4** and **5** survived the complexation procedure is $^{13}C$ NMR spectroscopy. The proton-decoupled $^{13}C$ spectrum of $[Ru(bpy)_2qpyme]^{3+}$ is shown in Figure 1A, and the frequencies of the resonances are summarized in Table I. The spectrum shows the expected 22 resonances, 5 for carbon on the 2 equivalent coordinated bipyridines, and 17 on the methylated quaterpyridyl, including 1 for the methyl group at 49.6 ppm. Integration of the $^1H$ spectrum of $[Ru(bpy)_2qpyme]^{3+}$ (not shown) indicates that there are 3 methyl

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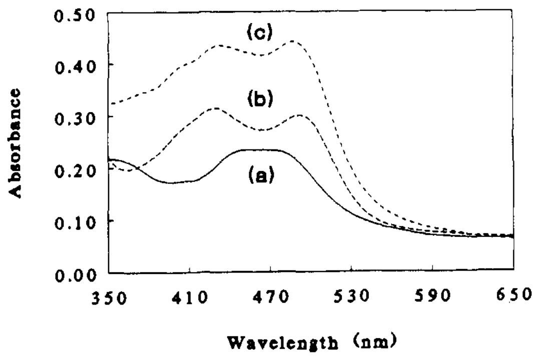

**Figure 2.** Electronic absorption spectra of (a) $[Ru(bpy)_2qpy]^{2+}$, (b) $[Ru(bpy)_2(qpyme_2)]^{4+}$, and (c) $[Ru(bpy)_2qpyme]^{3+}$.

**Table II.** Absorption Spectral Data

| complex | $\lambda_{max}$, nm | $10^4\epsilon$ | solvent |
|---|---|---|---|
| $[Ru(bpy)_2qpy]^{2+}$ | 473 | 2.3 | MeOH |
| | 429 | | |
| | 357 | 2.1 | |
| | 306 (sh) | | |
| | 289 | 7.8 | |
| | 252 | 11 | |
| $[Ru(bpy)_2qpyme]^{3+}$ | 487 | 1.3 | MeOH |
| | 430 | 1.3 | |
| | 310 (sh) | | |
| | 286 | 6.4 | |
| | 248 | 6.6 | |
| $[Ru(bpy)_2(qpye_2)]^{4+}$ | 492 | 1.4 | MeOH |
| | 430 | 1.5 | |
| | 330 | 1.9 | |
| | 285 | 6.1 | |
| | 253 | 5.2 | |

protons (singlet $\delta$ 4.44, 3 H) and 30 pyridine protons. Thus the $^{13}C$ and $^1H$ spectra agree with the structure proposed for $[Ru(bpy)_2qpyme]^{3+}$. The $^{13}C$ spectrum of $[Ru(bpy)_2(qpyme_2)]^{4+}$ is shown in Figure 1B, and the frequencies of the resonances are summarized in Table I. The spectrum shows a total of 14 resonances, 1 for the 2 equivalent methyl groups (49.6 ppm), 5 for the bipyridine carbons, and 8 for the aromatic carbons on the bis-methylated quaterpyridyl. The $^1H$ NMR spectrum (not shown) shows a singlet ($\delta$ 4.45, 6 H) for the 6 aliphatic protons and a 30-H multiplet in the aromatic region. The $^{13}C$ and $^1H$ NMR spectra are consistent with the structure $[Ru(bpy)_2(qpyme_2)]^{4+}$. Microanalysis of $[Ru(bpy)_2qpy]^{2+}$ falls within acceptable limits (see Experimental Section).

**Absorption Spectra.** All three complex ions, $[Ru(bpy)_2qpy]^{2+}$, $[Ru(bpy)_2qpyme]^{3+}$, and $[Ru(bpy)_2(qpyme_2)]^{4+}$, absorb strongly in the visible and the ultraviolet regions of the spectrum. Their spectra are shown in Figure 2, and their spectra data are summarized in Table II. As the number of quaternary methyl groups on the coordinated quaterpyridyl is increased, the low-energy band undergoes a shift to the red. The maximum occurs at 473 nm for $[Ru(bpy)_2qpy]^{2+}$, at 487 nm for $[Ru(bpy)_2qpyme]^{3+}$, and at 492 nm for $[Ru(bpy)_2(qpyme_2)]^{4+}$. All three complexes have an additional band in the visible at approximately 430 nm. The band is better resolved in the spectra of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ than in $[Ru(bpy)_2qpy]^{2+}$, where it overlaps the band at 473 nm.

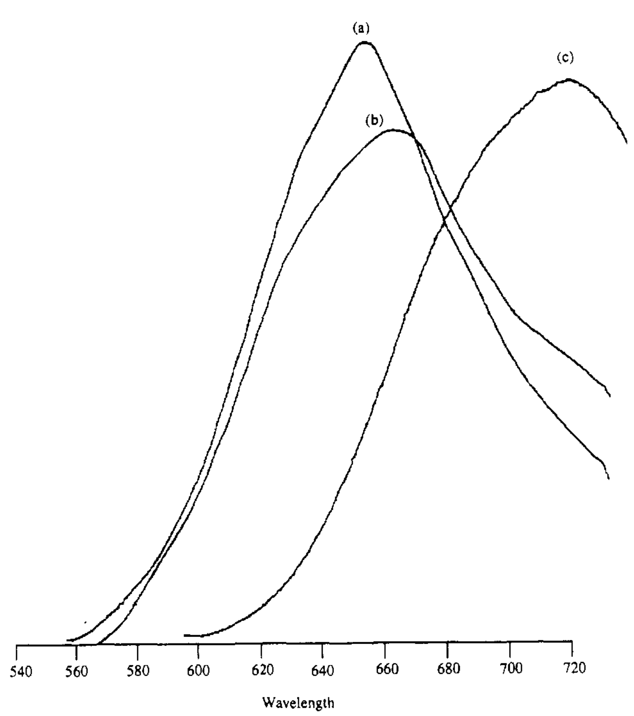

**Figure 3.** Emission spectra of (a) $[Ru(bpy)_2qpy]^{2+}$, (b) $[Ru(bpy)_2qpyme]^{3+}$, and (c) $[Ru(bpy)_2(qpyme_2)]^{4+}$ in water at 25° C, with $\lambda_{ext}$ = 500 nm.

**Table III.** Luminescence Data

| complex | $\lambda_{max}$, nm | $\phi_{max}$ | conditions[a] |
|---|---|---|---|
| $[Ru(bpy)_2qpy]^{2+}$ | 650 | 0.078 | 25 °C, $CH_3CN$ |
| | 660 | 0.053 | 25 °C, $H_2O$ |
| | 615 (sh 660) | | 77 K, MeOH/EtOH |
| $[Ru(bpy)_2qpyme]^{3+}$ | 665 (sh 715) | [0.0025][b] | 25 °C, $CH_3CN$ |
| | 670 | [0.0020][b] | 25 °C, $H_2O$ |
| | 650 | | 77 K, MeOH/EtOH |
| $[Ru(bpy)_2(qpyme_2)]^{4+}$ | 728 | 0.0054 | 25 °C, $CH_3CN$ |
| | 728 | 0.0013 | 25 °C, $H_2O$ |
| | 655 | | 77 K, MeOH/EtOH |
| $[Ru(bpy)_3]^{2+}$ | 608 | 0.062 | 25 °C, $CH_3CN$ |
| | 608 | 0.042 | 25 °C, $H_2O$ |

[a] Deaerated solutions unless otherwise stated. [b] The values are uncertain; see text.

**Table IV.** Excited-State Data

| complex | $\tau$, ns | $10^{-4}k_r$, $s^{-1}$ | $10^{-4}k_{nr}$, $s^{-1}$ | $10^{-4}(k_r + k_{nr})$, $s^{-1}$ | conditions[a] |
|---|---|---|---|---|---|
| $[Ru(bpy)_2qpy]^{2+}$ | 1418 | 5.5 | 71 | 76 | $CH_3CN$ |
| $[Ru(bpy)_2(qpyme_2)]^{4+}$ | 63 | 4.0 | 1600 | 1600 | $CH_3CN$ |
| | 68 | 1.9 | 1500 | 1500 | $H_2O$ |
| $[Ru(bpy)_3]^{2+}$ [b] | 860 | 7.2 | 110 | 117 | $CH_3CN$ |

[a] All solutions are degassed and at 25 °C unless otherwise stated. [b] Values taken from ref 2a.

**Emission Spectra.** All three complexes are luminescent in fluid solution at room temperature (Figure 3), and the emission data are summarized in Table III. $[Ru(bpy)_2qpy]^{2+}$ luminesces strongly with a maximum at 660 nm in water, and the emission maximum is slightly blue-shifted in acetonitrile solution. The emission quantum yield is 0.078 in acetonitrile and 0.053 in water, both higher than those observed for $[Ru(bpy)_3]^{2+}$ under the same conditions ($\Phi_{em}$ = 0.062[17] and $\Phi_{em}$ = 0.042[18]). $[Ru(bpy)_2(qpyme_2)]^{4+}$ shows a weak emission in both acetonitrile ($\Phi_{em}$ = 0.0054) and water ($\Phi_{em}$ = 0.0013), and the maximum occurs at 728 nm in both solvents. We are currently unable to report with confidence the quantum yield and excited-state lifetime for $[Ru(bpy)_2qpyme]^{3+}$. Samples which satisfy all the normal criteria for analytical purity are found to emit very weakly, on the order of that observed for $[Ru(bpy)_2(qpyme_2)]^{4+}$. However, the emission does not decay exponentially in either acetonitrile or water. Since luminescence is such a sensitive technique, we are unable to rule out the possibility that traces of the highly emissive $[Ru(bpy)_2qpy]^{2+}$ are present. For example, the possibility exists that a certain fraction of the $[Ru(bpy)_2qpyme]^{3+}$ sample self-reacts to give $[Ru(bpy)_2qpy]^{2+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$, which could be facilitated by laser excitation. The presence of even minute

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**Table V.** Electrochemical and Redox Data[a]

| | oxidation | | reductions | | | | excited state | | |
|---|---|---|---|---|---|---|---|---|---|
| complex | $E_{1/2}$ | $\Delta E_p$[b] | $E_{1/2}(1)$ | $\Delta E_p$ | $E_{1/2}(2)$ | $\Delta E_p$ | $E(A^+/A^*)$[c] | $E(A^*/A^-)$[c] | $E^{0-0}$ |
| $[Ru(bpy)_2qpy]^{2+}$ | 1.24 | 0.13 | −1.09 | 0.14 | −1.44 | 0.24 | −0.67 | 0.82 | 1.91 |
| $[Ru(bpy)_2qpyme]^{3+}$ | 1.37 | 0.10 | −0.73 | 0.11 | −0.91 | 0.12 | −0.49 | 1.13 | 1.86 |
| $[Ru(bpy)_2(qpyme_2)]^{4+}$ | 1.48 | 0.10 | −0.70 | 0.11 | −0.82 | 0.13 | −0.38 | 1.00 | 1.70 |
| $[Ru(bpy)_3]^{2+}$ | 1.29[d] | 0.95[e] | −1.33[f] | 0.10[e] | | | −0.81[g] | 0.84[g] | 2.1 |

[a] All potentials in V vs SCE. [b] Difference in peak potentials for forward and reverse scans are not corrected for cell resistence. [c] Excited-state potentials. [d] Reference 25. [e] As measured on our experimental setup. [f] Reference 26. [g] Reference 27.

quantities of $[Ru(bpy)_2qpy]^{2+}$ could introduce large errors in measurement of quantum yield and lifetime, the problem being more severe for the latter.

**Excited-State Lifetimes.** Excited-state lifetimes in acetonitrile are given in Table IV. The lifetime of $[Ru(bpy)_2qpy]^{2+}$ in acetonitrile is 1418 ns, and that for $[Ru(bpy)_2(qpyme_2)]^{4+}$ is 63 ns. The traces obtained for $[Ru(bpy)_2qpyme]^{3+}$ are nonexponential in acetonitrile, having two components of 1453 and 75 ns. These values are reported with the reservations stated above. Traces measured in water for both $[Ru(bpy)_2qpy]^{2+}$ and $[Ru(bpy)_2qpyme]^{3+}$ are also nonexponential. This is likely due to the presence of the free pyridine nitrogens on the coordinated quaterpyridyl, which allow the possibility of acid–base equilibria in aqueous solution. For example, the lifetime of $[Ru(bpy)_2qpy]^{2+}$ at pH 2 is markedly shorter than that obtained at pH 7 (on the order of 200 and 600 ns, respectively).

**Electrochemical Measurements.** Cyclic voltammograms for the three complexes are shown in Figure 4. Both the reduction and oxidation waves of the three complexes were determined to be one-electron events using the criteria of Polcyn and Shain.[19] The electrochemical data are summarized in Table V. The first reduction of $[Ru(bpy)_2qpy]^{2+}$ occurs at −1.09 V. The free quaterpyridyl has a lower reduction potential than that of bpy, and this reduction at −1.09 V can therefore be assigned to be localized on the coordinated qpy. The second reduction in Figure 4a is assigned to the first reduction of bpy in $[Ru(bpy)_2qpy]^{2+}$. Since the free ligand does not undergo oxidation below +2 V, the oxidation wave at +1.24 V is inferred to be metal centered.

The cyclic voltammogram of $[Ru(bpy)_2qpyme]^{3+}$ is shown in Figure 4a. The first two reduction waves occur at −0.73 and −0.91 V. Since both values are of lower potential than the first reduction of $[Ru(bpy)_3]^{2+}$ (Table V), as well as the second reduction of $[Ru(bpy)_2qpy]^{2+}$, both occur on the coordinated methylquaterpyridyl, as the reduction of a bipyridine would occur at considerably lower (more negative) potential. It is uncertain whether the third wave at −1.20 V represents a further reduction of methylquaterpyridyl or the first reduction of bipyridine. The Ru(II)/Ru(III) couple at +1.37 V occurs at slightly higher potential than in $[Ru(bpy)_2qpy]^{2+}$.

The cyclic voltammogram of $[Ru(bpy)_2(qpyme_2)]^{4+}$ is shown in Figure 4b. Its shape suggests that the first two reduction have similar potentials. It has been shown[19] that complete resolution into two distinct waves is not possible if the peak to peak potential difference is less than ~118 mV. We estimate that the spacing of the first two reduction waves in the voltammogram of $[Ru(bpy)_2(qpyme_2)]^{4+}$ is ~120 mV and are therefore only able to obtain approximate $E^{\circ\prime}$ values of −0.70 and −0.82 V for the first two reduction waves. Both represent reductions of the coordinated dimethylquaterpyridyl. While the first reductions of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ occur at the same potential, the second reduction in $[Ru(bpy)_2(qpyme_2)]^{4+}$ occurs at a lower potential than the corresponding reduction in $[Ru(bpy)_2qpyme]^{3+}$. The presence of the second quaternized pyridine ing in $[Ru(bpy)_2(qpyme_2)]^{4+}$ lowers the second reduction potential by providing another viologen-like reduction site. Again, the assignment of waves at higher (more negative) potential is uncertain. The Ru(II)/Ru(III) couple occurs at $E^{\circ\prime}$ = 1.48 V.

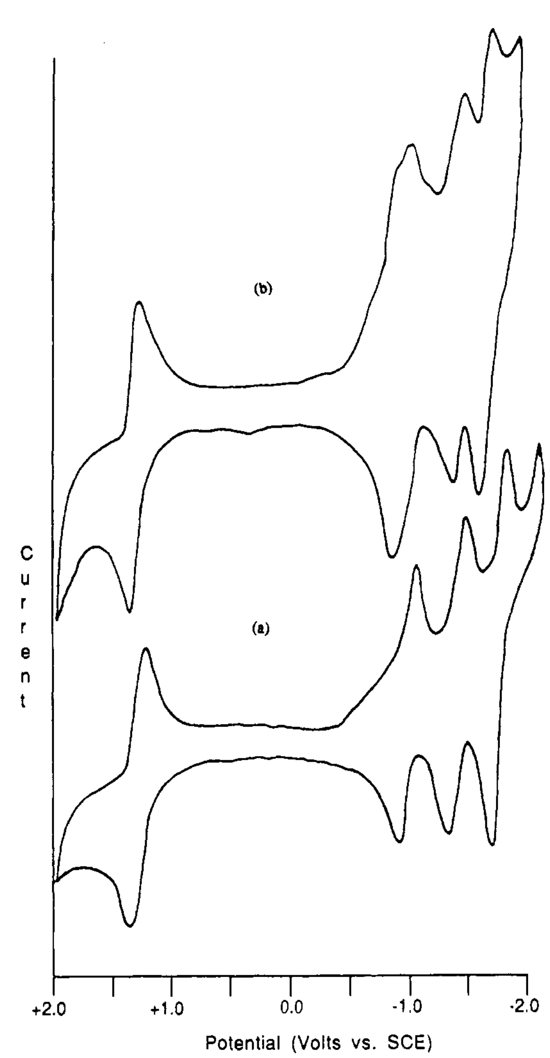

**Figure 4.** Cyclic voltammograms of (a) $[Ru(bpy)_2qpyme]^{3+}$, and (b) $[Ru(bpy)_2(qpyme_2)]^{4+}$ in $CH_3CN$. Potentials are versus SCE, 200 mV/s, with a Pt-disk working electrode.

**Resonance Raman Spectra.** Resonance Raman spectra at two different excitation wavelengths are shown in Figure 5. Excitation of $[Ru(bpy)_2(qpyme_2)]^{4+}$ at 457.9 nm (at approximately the midpoint between the absorptions bands at 430 and 492 nm) results in enhancement of bpy[20] vibrations at 1562, 1490, 1323, and 1177 cm$^{-1}$. For excitation at 488.0 nm, bands at 1648, 1619, 1542, 1339, and 1260 cm$^{-1}$ are enhanced and can be inferred to be vibrations of chelated $qpyme_2^{2+}$. A similar result is obtained for $[Ru(bpy)_2qpyme]^{3+}$. Excitation at 457.9 nm enhanced bpy vibrations at 1564, 1490, 1324, and 1175 cm$^{-1}$, as compared to the spectrum that results from 488.0-nm excitation. The $qpyme^+$ vibrations are assigned to bands occuring at 1648, 1619, 1543, 1339, 1287, and 1256 cm$^{-1}$. The resonance Raman spectrum of $[Ru(bpy)_2qpy]^{2+}$ is very similar to that of $[Ru(bpy)_3]^{2+}$, with only minor bands at 1617 and 1254 cm$^{-1}$ and a medium-intensity band at 1534 cm$^{-1}$ assignable to coordinated qpy. The resonance Raman spectrum of $[Ru(qpy)_3]^{2+}$ indicates that a strong band at about 1481 cm$^{-1}$ is due to qpy, only 9 cm$^{-1}$ below an equally strong bpy

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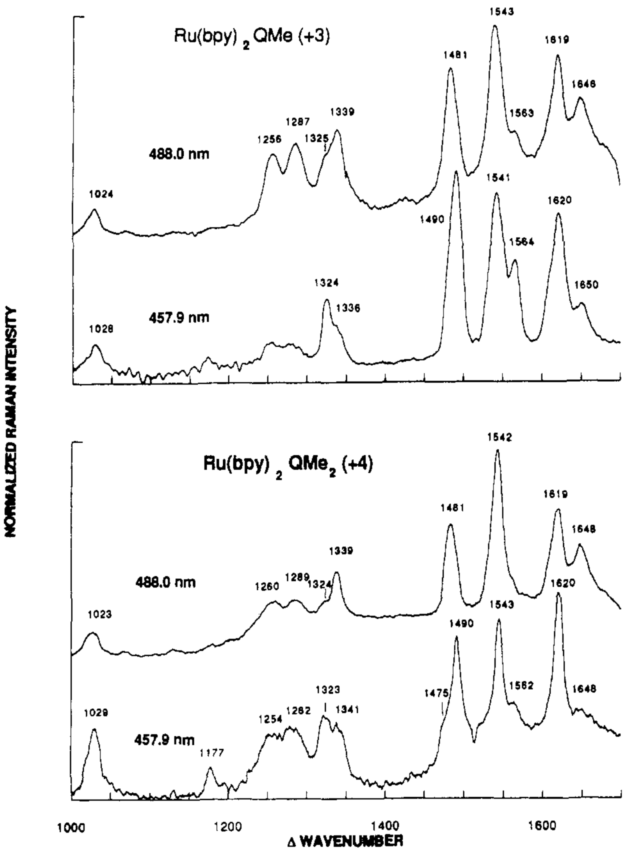

**Figure 5.** Resonance-enhanced Raman spectra of ca. 5 × $10^{-4}$ M aqueous solutions of $[Ru(bpy)_2qpyme]^{3+}$ (top) and $[Ru(bpy)_2(qpyme_2)]^{4+}$ (bottom) using 488.0- and 457.9-nm excitation.

band, seen in resonance Raman spectra of all bpy complexes. The 1490-cm$^{-1}$ bpy band is notable in the 457.9-nm spectra reported here whereas the 1481-cm$^{-1}$ (substituted qpy) band is notable in the 488-nm spectra (i.e. the 9-cm$^{-1}$ difference is consistently observed). Enhancement of the bpy pattern of vibrations upon excitation of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ at 457.9 nm, in conjunction with the enhancement of qpyme$^+$ and qpyme$_2{}^{2+}$ vibrations with 488.0-nm excitation, allows the assignment of the long-wavelength transitions in the absorption spectra of $Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ as transitions which terminate on orbitals located on qpyme$^+$ and qpyme$_2{}^{2+}$ ligands, respectively. The absorption bands at 430 nm in $[Ru(bpy)_2qpyme]^{3+}$ and at 429 nm in $[Ru(bpy)_2(qpyme_2)]^{4+}$ are assigned as a MLCT transition to a coordinated 2,2′-bipyridine.

## Discussion

**Absorption Spectra.** Absorption bands in the visible region (>400 nm) of ruthenium(II) diimine complexes are due to spin-allowed $^1$(MLCT) transitions. In tris($\alpha$-diimine) heteroleptic complexes of the type $[Ru(bpy)_2L]^{2+}$, MLCT bands to both ligands can be observed if the energy difference of the bands is large enough to permit their resolution. The band for the coordinated bpy can usually be observed between 420 and 430 nm. The two bands are barely resolved in the spectrum of $[Ru(bpy)_2qpy]^{2+}$, as they are nearly equal in intensity, and merge into a broad band with two barely discernible maxima at 473 and 429 nm. Quaternization on the remote quaterpyridyl lowers the energy of the transition to that ligand, producing an increased resolution of the bands in the spectra of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$.

**Electrochemistry.** The single reversible oxidation wave for $[Ru(bpy)_3]^{2+}$ has been assigned to the removal of an electron from a metal-centered $t_2$ orbital.[21,22] The oxidation wave for $[Ru(bpy)_2qpy]^{2+}$ is at a potential similar to the accepted value for $[Ru(bpy)_3]^{2+}$ (1.28 V vs SCE in acetonitrile).[2a] This suggests that the energies of the metal d orbitals are not significantly perturbed by the additional pyridine functionalities of the quaterpyridyl. The oxidation potentials of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ are shifted to more positive values (+1.37 and +1.48 V, respectively).

It has been generally observed that the electrochemical potentials of related $[Ru(bpy)_2L]^{2+}$ complexes shift to the positive side as the electron-withdrawing character of the ligand L is increased. Electrochemical studies on the free ligands **3**–**5** suggest that the LUMOs of the free ligands are lowered as a result of quaternization. The free diquaternary salt shows two reduction waves at −0.78 and −0.86 V, the monoquaternary salt shows a single wave at −0.79 V, and the free quaterpyridyl cannot be reduced below −1.7 V. These results closely parallel those for the bis(bipyridine) complexes of ligands **3**–**5**. The first two reductions in $[Ru(bpy)_2(qpyme_2)]^{4+}$ (−0.70 and −0.82 V) and the first in $[Ru(bpy)_2qpyme]^{3+}$ (−0.73 V) all occur on the quaterpyridyl ligands, and because their potentials are very similar to those obtained on the free ligands, we conclude that the viologen sites in $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ remain largely undisturbed by the metal center.

**Excited-State Behavior.** The lowest excited state of $[Ru(bpy)_3]^{2+}$ is considered to be composed of four closely spaced states which are considered to be of triplet multiplicity $^3$(MLCT). The spacing of these $^3$(MLCT) states is small, and they require low temperatures to be resolved.[23] At room temperature they may be considered to be effectively a single state. The decay from this manifold of $^3$(MLCT) states[24] can occur by luminescence ($k_r$), by nonradiatively ($k_{nr}$), or through a temperature-dependent surface crossing to a $^3$(MC) state or states. Experimentally $k_r$ and $k_{nr}$ can be obtained from lifetime and quantum yield measurements, and the contribution of decay through a $^3$(MC) from a temperature dependence of the lifetime study.

The radiative rate constants for $[Ru(bpy)_2qpy]^{2+}$, $[Ru(bpy)_3]^{2+}$, and $[Ru(bpy)_2(qpyme_2)]^{4+}$ are similar in acetonitrile. The nonradiative rate constants for $[Ru(bpy)_2qpy]^{2+}$ and $[Ru(bpy)_3]^{2+}$ are again similar, while that for $[Ru(bpy)_2(qpyme_2)]^{4+}$ is considerably larger.

It is imprudent to compare the excited-state decays of these complexes too closely. The charges on the periphery of $[Ru(bpy)_2(qpyme_2)]^{4+}$ present several difficulties. The resonance Raman results of these and related Ru(II) heteroleptic/$\alpha$-diimine complexes indicate the excited state has enhanced electron density on the ligand with the lowest LUMO energy; e.g., in the case of $[Ru(bpy)_2(qpyme_2)]^{4+}$ the enhanced electron density would lie on the *N*,*N*′-dimethylquaterpyridinium ligand. The MLCT transition to this ligand will result in an excited state which has a Ru(III) core and a singly *positive* acceptor ligand. To our knowledge, all other excited ruthenium(II)/$\alpha$-diimine complexes studied to date are composed of a Ru(III) core and a *negative* or *neutral* acceptor ligand. It is interesting that the values of $k_{nr}$ for $[Ru(bpy)_2(qpyme_2)]^{4+}$ are very similar in both water and acetonitrile. Coupling to the O–H vibration of water apparently does not significantly alter the mechanism of excited-state decay in the protic solvent. The mechanism by which a cationic excited state would dissipate energy through the solvent is likely to be different, and this difference could manifest itself in atypical values of $k_{nr}$, compared to otherwise similar excited ruthenium(II) $\alpha$-diimine complexes.

**Excited-State Potentials.** Excited-state potentials of the three complexes are listed in Table V. Those of $[Ru(bpy)_2qpy]^{2+}$ are high enough to make the complex a viable candidate for participation in excited-state redox schemes. In addition, the complex

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possesses two free pyridine rings which could be used to modify the rates of electron transfer using the free nitrogen atoms to interact with a suitable quencher. For the series of bis(bipyridine) complexes of ligands **3**–**5**, the complex ions become progressively poorer excited-state reductants but more potent excited-state oxidants. The excited-state redox potentials of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ indicate the complexes are poorer reductants in the excited state than $[Ru(bpy)_3]^{2+}$ but more potent excited-state oxidants.

## Conclusion

We report the preparation of a series of ruthenium complexes based on the quaterpyridyl ligand **3**. The complex $[Ru(bpy)_2qpy]^{2+}$ is strongly luminescent, has excited-state properties similar to those of $[Ru(bpy)_3]^{2+}$, and is an excellent candidate for use in energy conversion schemes. The complexes $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ demonstrate how simple modifications of the ground-state structure, quaternization on the remote pyridine nitrogens of $[Ru(bpy)_2qpy]^{2+}$, can have a large effect on excited-state properties.

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# Preparation, Structure, and Properties of the Bis($\mu$-acetato)($\mu$-oxo)Ruthenium(III) Dimers $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$

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Two ruthenium(III) dimers with a core structure similar to the methemerythrin active center have been prepared: $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ (**1**) and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ (**2**) (py = pyridine, bpy = 2,2'-bipyridine). $[Ru_2(CH_3COO)_2(O)(py)_6](PF_6)_2$ crystallizes in the monoclinic space group $C2/c$ with $a = 42.229$ (6) Å, $b = 10.726$ (1) Å, $c = 20.470$ (3) Å, $\beta = 112.45$ (1)°, $V = 8568$ (2) Å$^3$, and $Z = 8$. The Ru–Ru distance is 3.251 (2) Å, and the direct metal–metal bond is absent. $^1H$ NMR spectra of **1** in organic solvents are consistent with the solid-state structure. Those of **2** indicate that chelating bpy occupies the positions trans to the two acetate bridges. The complexes exhibit strong visible absorption bands at 581 nm ($\epsilon = 10\,000\ M^{-1}\ cm^{-1}$) and 599 nm ($\epsilon = 19\,200$) in $CH_3CN$ for **1** and **2**, respectively. Cyclic voltammograms of both complexes in $CH_3CN$ show one reversible oxidation process and one irreversible reduction process in the range from −1 to +1 V vs $Ag/AgClO_4$. The substitution reaction of py-$d_5$ for the coordinated py in **1** shows that the position trans to the oxide bridge is at least 10 times more labile than the cis positions. The first-order rate constants in the presence of excess py-$d_5$ (0.125 mol dm$^{-3}$) are $2.2 \times 10^{-4}$ and $5.5 \times 10^{-5}\ s^{-1}$ for **1** and **2**, respectively, at 50 °C in $CD_3CN$.

## Introduction

Dinuclear complexes with the $M_2(\mu\text{-}RCOO)_2(\mu\text{-}O)$ core[2] are now known for various first-row transition-metal ions, Ti(III),[3] V(III),[4] Mn(III),[5] and Fe(III)[6] and appear to be common to tervalent and also to some quadrivalent[7,8] metal ions as well as to the mixed-valence (III,IV) state.[5a,9] Mixed-metal dinuclear complexes with this core have also been reported.[10,11] These complexes are interesting not only from a purely chemical but also from a biochemical point of view, since the core is found in some iron and manganese enzymes.[5a,6a] Terdentate ligands such as 1,4,7-triazacyclononane and hydrotris(pyrazolyl)borate have been used in most cases to block the facial position of a metal ion to make favorable situation for the preparation of the face-shared dinuclear complexes.[5a,6a]

Studies of the trinuclear ruthenium complexes $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ ($L = H_2O$, pyridine (py)) and their derivatives showed that the Ru–Ru interaction through the central oxide ion is more significant than the metal–metal interactions in the similar trinuclear complexes of the first-transition-metal ions.[12-14] Electronic transitions, redox, and magnetic properties of the ru-

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