

# Generation by Electron Transfer of an Emitting State Not Observed by Photoexcitation in a Linked $\text{Ru}(\text{bpy})_3^{2+}$ –Methyl Viologen

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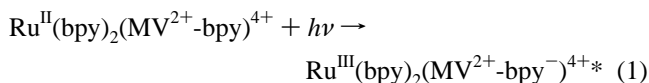
Received May 24, 1995<sup>⊗</sup>

**Abstract:** The molecule in which a methyl viologen ( $\text{MV}^{2+}$ ) moiety is coupled through a three-carbon chain to one bipyridine in  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\text{bpy} = 2,2'$ -bipyridine),  $[\text{Ru}(\text{bpy})_2(4-(2-(1'-methyl-4-4'-bipyridinedium-1-yl)propyl)-4'-methyl-2,2'-bipyridine)]$ , abbreviated  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$ , does not emit upon photoexcitation because of rapid quenching of the MLCT state by the  $\text{MV}^{2+}$ . The integrated steady-state photoemission intensity is  $<1/1000$  that of  $\text{Ru}(\text{bpy})_3^{2+}$  under the same conditions. However, quite efficient emission [ $\sim 1/5$  that of  $\text{Ru}(\text{bpy})_3^{2+}$ ] is found when  $\text{Ru}^{\text{III}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{5+}$  is electrogenerated at a Pt electrode in aqueous solution and reacts with a suitable coreactant (tri-*n*-propylamine or oxalate), where the excited state is produced by an electron-transfer reaction. Electrogenerated chemiluminescence is also observed for this species in acetonitrile solutions upon potential cycling via annihilation of the reduced (+1) and oxidized (+5) species.

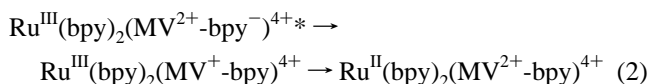
## Introduction

The luminescence and photochemistry of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\text{bpy} = 2,2'$ -bipyridine) and related species have been investigated intensively.<sup>1</sup> Emission has been shown to occur from a metal–ligand charge transfer (MLCT) state with a quantum efficiency at room temperature of about 0.04. The excited state can be quenched by electron acceptors, either free in solution or covalently linked to one of the bpy ligands. For example, previous studies of the photoexcitation of  $\text{Ru}(\text{bpy})_3^{2+}$  linked by a carbon chain to a methyl viologen ( $\text{MV}^{2+}$ ) moiety have shown that the MLCT state is rapidly quenched by intramolecular electron transfer to produce the ground state.<sup>2,3</sup> This process can be schematically represented as follows:

Excitation:

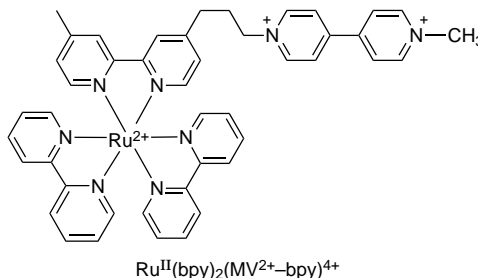


Quenching and back reaction:

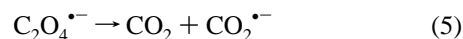
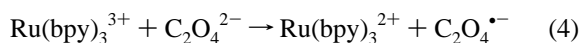
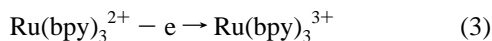


For the species under consideration here, abbreviated  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$ , with a three-carbon chain linker, the integrated steady-state photoemission intensity in aqueous buffered solution (pH 7.4) is less than 1/1000 that of the unmodified  $\text{Ru}(\text{bpy})_3^{2+}$ .

The excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  can also be generated by an electron-transfer process between the oxidized form,  $\text{Ru}(\text{bpy})_3^{3+}$ , and a strong reductant, R (where R is  $\text{Ru}(\text{bpy})_3^+$ ,  $\text{CO}_2^{\bullet-}$ , or  $\text{Pr}_2\text{NC}\cdot\text{HEt}$ ).<sup>4–7</sup> These are usually generated at an electrode,



e.g., by oxidizing  $\text{Ru}(\text{bpy})_3^{2+}$  in the presence of a suitable coreactant (e.g., oxalate) in a process called electrogenerated chemiluminescence (ECL):



We demonstrate here that an emitting excited state of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  can be generated by an ECL process. This finding leads to a deeper insight into the details of excited state production by electron-transfer processes.

## Experimental Section

**Apparatus.** An Origen I analyzer (IGEN, Inc., Rockville, MD) controlled by an IBM PS/2 computer was used to study the ECL emission in aqueous solutions. ECL experiments in acetonitrile utilized a glassy carbon working electrode (area = 0.071 cm<sup>2</sup>), a silver reference electrode, and a platinum wire counter electrode. Potentials are reported with respect to the ferrocene/ferrocenium couple added to the acetonitrile solution following voltammetric scans of the ruthenium compounds alone. The signal was applied with a Model 175 universal programmer and a Model 173 potentiostat (Princeton Applied Research, Princeton, NJ), and the ECL emission was detected with a Model C1230 single-photon-counting system (Hamamatsu Corp., Bridgewater, NJ) with a Hamamatsu R928P PMT cooled to  $-15$  °C in a Model TE 308

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, April 1, 1996.

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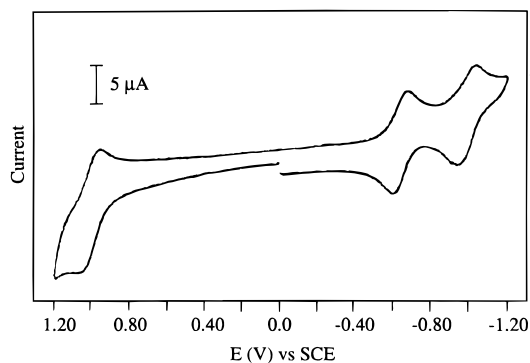
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**Figure 1.** Cyclic voltammogram of 0.6 mM  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  in 0.15 M phosphate buffer, pH 7, at a  $0.084 \text{ cm}^2$  glassy carbon electrode. The potential was scanned initially from 0 to 1.20 V; scan rate, 100 mV/s.

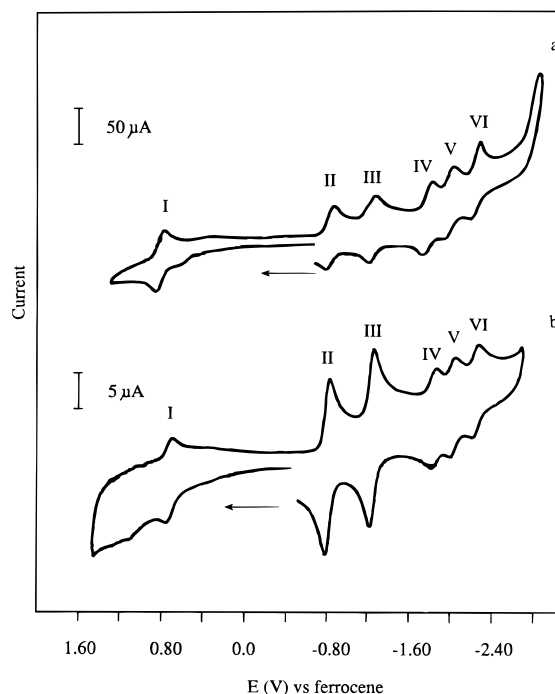
TSRF cooler controller (Products for Research Inc., Danvers, MA). The voltage to the preamplifier of the single-photon-counting system was adjusted to  $-750 \text{ V}$ , and the measuring time (gate time) for the emission input signal was set to 0.1 s. An SLM-AMINCO spectrofluorimeter, model SPF-500C (Urbana, IL), was employed to measure luminescence spectra. Electrochemical experiments were performed with a Bioanalytical Systems (West Lafayette, IN) Model BAS-100 electrochemical analyzer. A saturated calomel reference electrode (SCE) and a platinum wire counter electrode were used for all electrochemical measurements in aqueous solution. Bulk electrolysis experiments were carried out at a highly oriented pyrolytic graphite (HOPG) working electrode (area  $\sim 5 \text{ cm}^2$ ) with a platinum wire counter electrode in a separate compartment.

**Chemicals and Materials.**  $[\text{Ru}(2,2'\text{-bipyridine})_2(4\text{-}(2\text{-}(1'\text{-methyl-4-4'\text{-bipyridinediium-1-yl)-propyl})\text{-4'\text{-methyl-2,2'\text{-bipyridine}})]\text{-}(\text{NO}_3)_4$  was synthesized as described earlier.<sup>2</sup>  $\text{Ru}^{\text{II}}(\text{MV}^{2+}\text{-bpy})_3^{8+}$  was prepared according to the general procedure of Palmer and Piper<sup>8</sup> for the synthesis of  $\text{Ru}(\text{bpy})_3^{2+}$ . Both compounds gave satisfactory  $^1\text{H}$  NMR, UV–visible, low resolution (FAB) mass spectral, and elemental analyses (C, H, and N). The synthesis of  $\text{Ru}^{\text{II}}(\text{MV}^{2+}\text{-bpy})_3^{8+}$  is given in the supporting information.  $\text{Ru}(\text{bpy})_3\text{Cl}_2\cdot 6\text{H}_2\text{O}$  (Strem), tripropylamine (TPrA, Aldrich), methyl viologen chloride (Aldrich),  $\text{Na}_2\text{C}_2\text{O}_4$  (Baker),  $\text{NaH}_2\text{PO}_4$  (Baker), and tris(hydroxymethyl)aminomethane (Sigma) were used as received without purification.

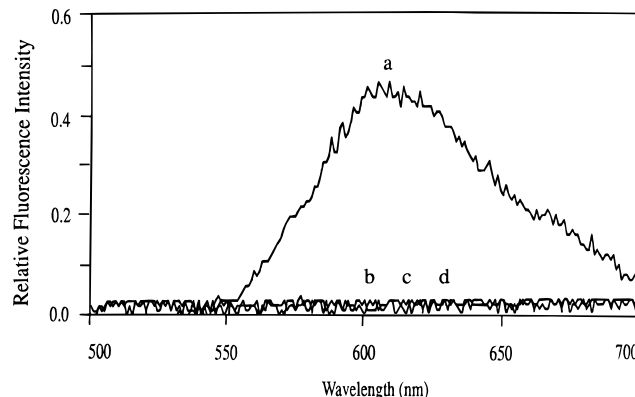
ECL experiments were carried out with a solution of 0.1 M TPrA and 0.1 M tris buffer, prepared by dissolving TPrA into a tris(hydroxymethyl)aminomethane solution with 1 M  $\text{H}_2\text{SO}_4$  and adjusting the pH to 7.0 with 1 M NaOH. An alternative solution contained 0.15 M TPrA and 0.2 M phosphate buffer, prepared by dissolving TPrA into a  $\text{NaH}_2\text{PO}_4$  solution with 1 M  $\text{H}_2\text{SO}_4$  and adjusting the pH to 7.4 with 1 M NaOH. The solutions for oxalate ECL experiments contained 25 mM  $\text{C}_2\text{O}_4^{2-}$  and 2 mM phosphate, prepared by dissolving  $\text{Na}_2\text{C}_2\text{O}_4$  in a  $\text{Na}_3\text{PO}_4$  solution and adjusting the pH to 5 with HCl. Deionized water from a Millipore Milli-Q ( $18 \text{ M}\Omega\cdot\text{cm}$ ) system was used to prepare all aqueous solutions. ECL results for these systems were qualitatively the same in the absence and presence of dissolved oxygen.

## Results and Discussion

**Electrochemistry.** A cyclic voltammogram of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  in an aqueous 0.15 M phosphate buffer (pH 7) at a glassy carbon electrode (Figure 1) shows two reduction waves ( $E_{p,r(1)} = -0.67 \text{ V}$ ;  $E_{p,r(2)} = -1.1 \text{ V}$  vs SCE) corresponding to the reduction of the  $\text{MV}^{2+}$  moiety to the +1 and 0 states. Oxidation occurred at  $+0.97 \text{ V}$  and corresponded to the formation of the  $\text{Ru}(\text{III})$  state. A representative cyclic voltammogram of 2.7 mM  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  in acetonitrile/0.2 M TBAPF<sub>6</sub> at a glassy carbon electrode is shown in Figure 2a. The waves can be assigned by comparison of the potentials to those found for  $\text{Ru}(\text{bpy})_3^{2+}$ <sup>3,4</sup> and  $\text{MV}^{2+}$  alone under similar conditions. The waves seen are for the oxidation of  $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$  (I) and the reduction of  $\text{MV}^{2+}$  (II, III), followed by the reduction of the bpy centers (IV, V, VI). All waves are



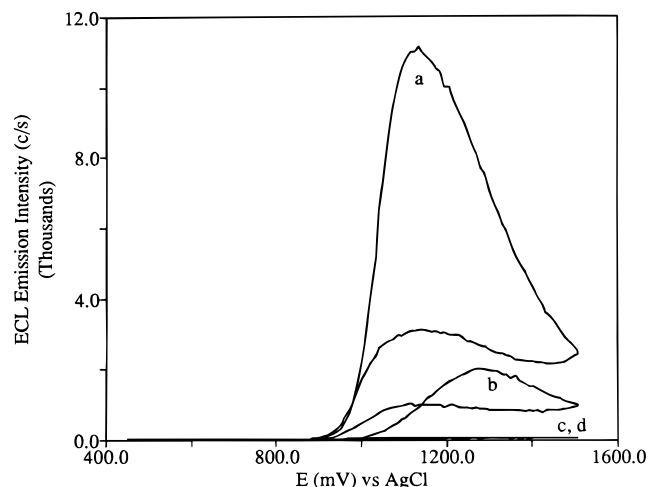
**Figure 2.** Cyclic voltammograms of (a) 2.7 mM  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  and (b) 0.24 mM  $\text{Ru}^{\text{II}}(\text{MV}^{2+}\text{-bpy})_3^{8+}$  in an acetonitrile solution containing 0.2 M TBAPF<sub>6</sub> supporting electrolyte at a glassy carbon electrode (area,  $0.071 \text{ cm}^2$ ). The potential was initially scanned from 0 to 2.0 V; scan rate, 100 mV/s.



**Figure 3.** Luminescence spectra in 0.2 M phosphate buffer, pH 7.4, containing 0.15 M TPrA: (a)  $3 \mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$ , (b)  $3 \mu\text{M}$   $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$ , (c)  $3 \mu\text{M}$   $\text{Ru}^{\text{II}}(\text{MV}^{2+}\text{-bpy})_3^{8+}$ , and (d) background. Excitation wavelength = 455 nm. Bandpass = 4 nm. The measurement sensitivity for b, c, and d was 100 times that for a (corrected for background).

of equal height, each equivalent to a one-electron transfer. Also shown for comparison purposes is the voltammogram for the species where all the bpy ligands contain a  $\text{MV}^{2+}$  moiety,  $\text{Ru}^{\text{II}}(\text{MV}^{2+}\text{-bpy})_3^{8+}$  (Figure 2b). Note that for this molecule the peak currents in the waves assigned to the  $\text{MV}^{2+}$  reductions (II, III) are significantly larger than those for the  $\text{Ru}^{\text{II}}$  oxidation or bpy reductions. This single, essentially 3-electron wave for both steps in the  $\text{MV}^{2+}$  reductions (to the  $\text{MV}^+$  and  $\text{MV}^0$  forms) is consistent with no interaction between the substituted  $\text{MV}^{2+}$  centers.<sup>9</sup> This can be contrasted with the more negative bpy reduction waves of  $\text{Ru}(\text{bpy})_3^{2+}$  and both compounds in Figure 2, where a sequence of one-electron waves is observed, signaling repulsive interactions among the bpy centers.

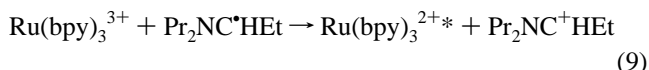
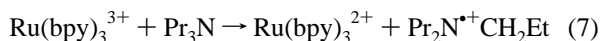
**Photoluminescence.** A comparison of the emission spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  with excitation at 455 nm (Figure 3) shows essentially complete quenching by the  $\text{MV}^{2+}$  substituent in an aqueous buffer. The addition of the 0.15 M TPrA used in ECL experiments did not significantly



**Figure 4.** ECL emission-potential transients at a platinum electrode in 0.2 M phosphate buffer, pH 7.4, containing 0.15 M TPrA: (a) 3  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$ , (b) 3  $\mu\text{M}$   $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$ , (c) 3  $\mu\text{M}$   $\text{Ru}^{\text{II}}(\text{MV}^{2+}\text{-bpy})_3^{8+}$ , and (d) background. Scans were initiated at 500 mV and directed toward more positive potentials. Scan rate, 500 mV/s.

affect the photoemission. Rapid intramolecular electron transfer quenching in  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  and related compounds was demonstrated previously.<sup>2,3</sup>

**Electrogenerated Chemiluminescence: Aqueous Coreactant System.** In contrast to the photoemission results, ECL emission is readily observed for  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  with either TPrA or  $\text{C}_2\text{O}_4^{2-}$  as coreactant. Typical results for 3  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  in 0.2 M phosphate buffer (pH 7.4) containing 0.15 M TPrA (Figure 4) show that the emission of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  is about  $1/5$  that of  $\text{Ru}(\text{bpy})_3^{2+}$  under the same conditions. With TPrA as coreactant, the proposed ECL mechanism<sup>6,7</sup> is eq 3 followed by



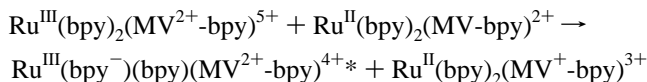
As with  $\text{Ru}(\text{bpy})_3^{2+}$ , the ECL emission intensity is linearly related to the  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  concentration (Figure S1 in the supporting information).

A number of experiments were carried out to rule out trivial explanations (impurities or decomposition) for the observed ECL emission. First, the buffer and coreactant were changed from phosphate buffer with oxalate coreactant to tris buffer with TPrA coreactant. Essentially the same ECL results were observed in all cases, verifying that the emission is an intrinsic feature of the  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  species and not uniquely dependent on the other moieties present. In addition, bulk electrolysis of the solution containing 0.43 mM  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  (0.2 M phosphate buffer, pH 7.4, containing 0.15 M TPrA) at 1.20 V vs SCE (HOPG electrode) was carried out for 6 h in a dry bag purged with Ar. Both  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  and TPrA were oxidized under these conditions, so the charge passed (3.1 C) was considerably larger than the theoretical amount for the one-electron oxidation of the Ru(II) center (0.21 C). No photoemission was observed for this solution under Ar following the bulk electrolysis, suggesting that electrolysis does not produce a new species (e.g.,  $\text{Ru}(\text{bpy})_3^{2+}$ ) that is luminescent (in the absence of generation of significant amounts of quencher).

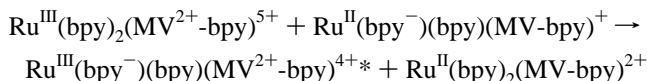
Finally, bulk electrolysis of a 0.6 mM  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  solution at  $-0.80$  V vs SCE in a closed, degassed cell (Ar purged glovebag, 0.15 M phosphate buffer, pH 7) produced a dark green solution that showed an absorbance peak at 608 nm, typical of the  $\text{MV}^{\bullet+}$  species. After the complete one-electron reduction ( $n_{\text{app}} = 0.94$  and 1.4 in two separate experiments), the solution showed no photoemission (excitation at 455 nm). These results verify that although it is possible that the  $\text{MV}^{2+}$  substituent is reduced in the ECL experiment by reaction of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  with  $\text{Pr}_2\text{NC}^+\text{HEt}$  or  $\text{CO}_2^{\bullet-}$ , this does not result in an emitting species.

**Electrogenerated Chemiluminescence: Acetonitrile Annihilation System.** ECL is also produced with the  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  in acetonitrile containing 0.2 M TBAPF<sub>6</sub> supporting electrolyte at a glassy carbon electrode in the annihilation mode. In this mode the electrode is pulsed between potentials where oxidized and reduced forms are produced alternately and undergo an electron-transfer reaction in the diffusion layer near the electrode.<sup>4</sup> Typical ECL emission-time responses are observed (Figure S2 in the supporting information). Emission is not observed when the electrode is pulsed between wave I,  $\text{Ru}^{\text{III}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{5+}$  production, and wave II,  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^+\text{-bpy})^{3+}$  (curve a), because the free energy difference for the electron-transfer reaction, about 1.7 eV, is too small to populate the emitting state at about 2.1 eV. However, emission is observed for pulsing between wave I and any of the more negative waves (III, IV, V, VI; Figure 2a). The proposed electron-transfer reactions are:

between I and III



and between I and IV

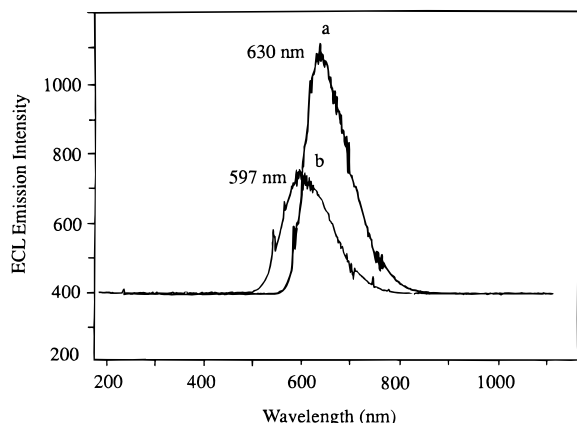


Thus the excited state arises by addition of an electron to the oxidized form by any of the reduced forms of sufficiently negative potential. These reduced species play the same role as the  $\text{CO}_2^{\bullet-}$  and  $\text{Pr}_2\text{NC}^+\text{HEt}$  used in the aqueous media.

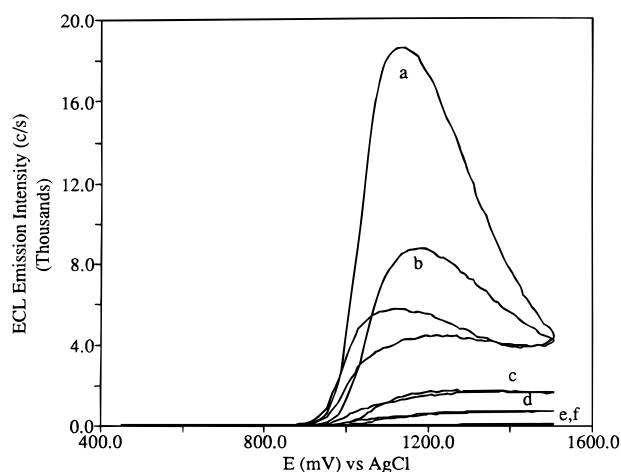
ECL also arises in acetonitrile solutions of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  (0.7 mM) containing 0.18 M TPrA and 0.1 M TBAPF<sub>6</sub> when a Pt electrode is stepped to potentials where both the  $\text{Ru}^{\text{II}}$  species and TPrA are oxidized (+1.8 V vs AgQRE). The ECL spectrum obtained by repeated pulsing (pulse width = 0.5 s) and integration of the emission with a CCD camera is shown in Figure 5. A comparison with the ECL spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$  taken under similar conditions shows the  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  ECL emission peak to be blue-shifted by about 33 nm. No ECL emission is observed in a blank experiment (0.18 M TPrA and 0.1 M TBAPF<sub>6</sub> in acetonitrile) under the same conditions.

**Quenching Experiments.** Although ECL emission is observed with  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$ , this emission, as well as that of  $\text{Ru}(\text{bpy})_3^{2+}$ , is quenched by adding  $\text{MV}^{2+}$ . Typical ECL transients for  $\text{Ru}(\text{bpy})_3^{2+}$  with TPrA in the presence of increasing amounts of  $\text{MV}(\text{ClO}_4)_2$  are shown in Figure 6. ECL of  $\text{Ru}(\text{bpy})_3^{2+}$  is similarly quenched with oxalate as a coreactant as is  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  with TPrA and oxalate. These results can be represented as Stern-Volmer-type plots ( $I_0/I$  vs  $[\text{MV}^{2+}]$ , where  $I_0$  is the ECL intensity in the absence of  $\text{MV}^{2+}$  and  $I$  is the intensity at a given concentration of added  $\text{MV}^{2+}$ ) (Figure S3 in the supporting information). The quenching of

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**Figure 5.** ECL spectra of (a) 2.9 mM  $\text{Ru}(\text{bpy})_3^{2+}$  and (b) 0.7 mM  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  in an acetonitrile solution containing 0.18 M TPrA and 0.1 M TBAPF<sub>6</sub> at a Pt electrode repeatedly pulsed between 0 and 1.8 V vs AgQRE (pulse width, 0.5 s) and recorded with a CCD camera. Total integration times: (a) 3 min; (b) 30 min.



**Figure 6.** ECL emission–potential transients at a platinum electrode in 0.2 M phosphate buffer, pH 7.4, containing 0.15 M TPrA: (a) 6  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  with (b) 0.5, (c) 2.4, (d) 4.8, and (e) 24 mM  $\text{MV}(\text{ClO}_4)_2$ , and (f) background. Scans were initiated at 500 mV and directed toward more positive potentials. Scan rate, 500 mV/s.

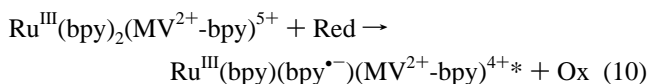
ECL of  $\text{Ru}(\text{bpy})_3^{2+}$  is somewhat more rapid compared to that of photoemission (Figure S3A,B). ECL quenching of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  occurs in the presence of either coreactant (Figure S3C). Clearly  $\text{MV}^{2+}$  is an efficient intermolecular electron transfer quencher, with emission decreased by at least one-half with millimolar amounts of added  $\text{MV}^{2+}$ .

**Mechanism.** One explanation for the reported results is that a luminescing impurity forms during the ECL process, e.g., by decomposition of the complex during its electrochemical oxidation. However, there is no evidence for such a process. We have shown here that ECL is observed under very different solution conditions, i.e., with two different coreactants in water and via annihilation and with a coreactant in acetonitrile. Moreover, examination of the solutions used in the ECL experiments or after even more extensive bulk electrolysis fails to show any photoluminescence.

Assuming the effect is not artifactual, we can think of several possible mechanisms that account for generation of an excited state by electron transfer that is not accessible by photoexcitation. One could involve different structural conformations of the excited state resulting from photoexcitation and electron transfer. For example, one could imagine that because of electrostatic interactions the  $\text{MV}^{2+}$  moiety is held further from the Ru center in the oxidized Ru(III) species than in the Ru(II) ground state, so that, at the instant of excitation via electron transfer, this center is not as well positioned for quenching.

However, given the relatively long lifetime of the MLCT excited state,  $\sim 600$  ns, conformational relaxation would occur before emission, leading to the same excited state configuration and quenching. Thus, a conformational basis for our results is unlikely.

An alternative mechanism for the observed emission in the ECL experiments is based on the electron-transfer reaction accessing an emitting excited state that is different than that quenched in photoexcitation experiments. In the electron transfer excitation reaction, e.g., eq 6, the unsubstituted bipyridine ligands are available to the strong reductant. Hence, at least to some extent, the following reaction occurs:



where Red represents the reducing agent (e.g.,  $\text{CO}_2^{\bullet-}$ ) and Ox its oxidation product (e.g.,  $\text{CO}_2$ ). Emission is proposed to occur from the  $\text{Ru}^{\text{III}}(\text{bpy})(\text{bpy}^{\bullet-})(\text{MV}^{2+}\text{-bpy})^{4+*}$  state. Direct electron transfer from the reductant to the substituted bpy and directly to the  $\text{MV}^{2+}$  can also occur, but presumably significant emission from the  $\text{Ru}^{\text{III}}(\text{bpy})(\text{bpy}^{\bullet-})(\text{MV}^{2+}\text{-bpy})^{4+*}$  state takes place before it is quenched.

There are three basic assumptions that must be true for relatively intense ECL emission to be observed from an intact  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  species by the proposed mechanism. First, the emitting  $^3\text{LMCT}$  state must involve an excited electron that is localized on a single bpy ligand. Second, efficient quenching by the  $\text{MV}^{2+}$  must occur only from an excited electron that is localized on the bpy covalently attached to the  $\text{MV}^{2+}$ . Third, an excited electron localized on an underivatized bpy ligand must not be able to hop onto the  $\text{MV}^{2+}\text{-bpy}$  ligand faster than the time scale of the emission. There is experimental evidence supporting the first two assumptions.<sup>10–14</sup> For example, a resonance Raman spectroscopic study of  $\text{Ru}^{\text{II}}(\text{bpy})_3\text{-}n$ -(DMB)<sub>n</sub> ( $n = 0\text{--}3$ ) (where DMB is 4,4'-dimethyl-2,2'-bipyridine) and its MLCT excited state concluded that the optically excited electron is localized on a ligand and “preferentially resides on a bpy ligand rather than on a DMB ligand on the vibrational time scale.” The third assumption involving the rate of electron transfer from ligand to ligand in these types of molecules (sometimes also called exciton hopping) has been controversial. We know of no direct measurements addressing ligand electron transfer in  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$ . Elliot, Kelley, and co-workers carried out a photophysical study using  $\text{Ru}^{\text{II}}$ -diquat systems with various bpy derivatives.<sup>10a</sup> The observed differences in excited state lifetimes between the different complexes were explained by assuming equilibration due to hopping of the excited electron between bpy ligands, and an estimated upper limit of 80 ps was placed on the time scale for this process. Similarly, Kelley and co-workers have employed picosecond polarized absorption spectroscopy of Ru-

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(bpy)<sub>3</sub><sup>2+</sup><sup>15</sup> and Os(bpy)<sub>3</sub><sup>2+</sup><sup>16</sup> to study the polarization decay of the excited states and interpreted these results to indicate rapid ( $\leq 100$  ps) interligand electron transfer and rotational diffusion. However, Hopkins and co-workers,<sup>17</sup> by employing picosecond Raman spectroscopy of Ru<sup>II</sup>(bpy)<sub>3-n</sub>(DMB)<sub>n</sub> and observing the spectra of the ground and excited states as a function of time, concluded that the electron-transfer rate between ligands was "very slow" ( $< 2 \times 10^6$  s<sup>-1</sup>). This latter measurement would be consistent with production of an excited state in the ECL experiment that emits before being quenched by interligand electron transfer.

Alternative explanations are possible, although, as discussed below, we feel they are less likely. For example, the ECL experiment could involve emission from a modified species, not Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup>. Alternatively, it might not be the emission, but rather the ECL excitation, that is more efficient compared with photoexcitation. These two possibilities will now be addressed individually.

It is possible that in the ECL experiment some impurity or ligand damage is temporarily produced that leads to an emissive species. In this case, the emissive moiety would have been gone before the photoexcitation experiment was carried out following bulk electrolysis. Although there is no direct evidence that refutes this possibility, the following observations make the temporary production of an emissive species unlikely. ECL experiments conducted with Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> in aqueous experiments produced roughly 20% of that observed with Ru(bpy)<sub>3</sub><sup>2+</sup> with a similar value in acetonitrile (Figure 5; note that the concentrations and integration times for the two species are different). These two experiments have no components in common except for the Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> itself. Thus, it appears the emission is an inherent property of Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> and not the product of some temporary species resulting from interactions with other components in the solution. Moreover, the very different solution conditions in the different ECL experiments suggest that the same chemistry leading to ECL emission is unlikely. Another alternative emitter is the reduced species Ru<sup>III</sup>(bpy)(bpy<sup>•-</sup>)(MV<sup>+</sup>-bpy)<sup>3+</sup> formed by two successive rapid electron transfers to the Ru<sup>III</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>5+</sup>. We showed that electrogenerated Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>+</sup>-bpy)<sup>3+</sup> does not photoemit. This is consistent with the known ability of reductant to quench excited states of ruthenium(II) bipyridine complexes. To the extent that excitation of Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>+</sup>-bpy)<sup>3+</sup> produces the MLCT state, Ru<sup>III</sup>(bpy)(bpy<sup>•-</sup>)(MV<sup>+</sup>-bpy)<sup>3+</sup> emission from this state does not occur. Moreover, we feel it is unlikely that the state Ru<sup>III</sup>(bpy)(bpy<sup>•-</sup>)(MV<sup>2+</sup>-bpy)<sup>4+</sup> would be sufficiently long-lived to undergo an additional electron-transfer reaction from another short-lived species like CO<sub>2</sub><sup>•-</sup>.

The alternative explanation for the observed emission is that the ECL excitation might be so efficient that even a highly quenched species such as Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> gives off some emission. This cannot be an explanation for our results, however, because the ECL emission of Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> is high relative to that of the well-characterized standard Ru(bpy)<sub>3</sub><sup>2+</sup>. Thus, to suggest that enhanced excitation is the correct explanation, we would have to argue that Ru(bpy)<sub>3</sub><sup>2+</sup> emission is somehow lower than expected relative to that from Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup>. In fact, Ru(bpy)<sub>3</sub><sup>2+</sup> ECL emission is linearly dependent on Ru(bpy)<sub>3</sub><sup>2+</sup> concentration up to much higher levels

(mM) than used in the experiments here, and independent earlier annihilation studies show a very high efficiency for Ru(bpy)<sub>3</sub><sup>2+</sup> ECL.<sup>18,19</sup>

Consideration of the proposed mechanism inspired the investigation of a new complex containing three MV<sup>2+</sup>-substituted bitys, Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup>. The electrochemical behavior of this species in acetonitrile was discussed earlier and is shown in Figure 2b. Oxidation of this species in aqueous solutions occurs at essentially the same potentials as that for Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup>. Experiments in aqueous solutions with Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup> carried out under virtually the same conditions as those with Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> show that no emission is observed under either photoexcitation or ECL conditions (Figures 3c and 4c). In acetonitrile solution, no ECL emission was observed with this species when the electrode was pulsed at potentials between wave I and waves II and III. However, some emission was seen for potentials between waves I and IV and beyond, but this emission decayed more quickly with time and was about one-tenth that found with Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup>. This result indicates that unmodified bipyridine ligands promote the ECL emission, consistent with the proposed mechanism. The small amount of emission from the Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup> species suggests that some decomposition of this species occurs at potentials where all three MV<sup>2+</sup> groups are reduced to the MV<sup>0</sup> state and an electron is then introduced into the bpy.

We have also found that related molecules, Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> and Ru(phen)<sub>2</sub>(dppz)<sup>2+</sup> (where dppz = dipyrido[3,2-*a*:2',3'-*c*]phenazine),<sup>20</sup> behave similarly, i.e., they show essentially no photoluminescence in aqueous solution, but produce ECL emission. These results will be reported elsewhere. The large difference in structure between the quenching moieties in these and Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> makes even the temporary damage of quenchers or artifacts an unlikely cause for the observed ECL emission in these species.

## Conclusion

The ECL emission of Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> in aqueous and acetonitrile solutions under conditions where photoluminescence is not observed demonstrates that excited states are accessible via electron-transfer reactions that cannot be produced by photons. This concept is analogous to previous studies that showed that triplet states of 9,10-diphenylanthracene and rubrene could be generated by the ECL mode, although they are not formed by photoexcitation via the excited singlets, which luminesce with essentially unit quantum efficiency.<sup>21-23</sup>

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**Supporting Information Available:** Synthesis of Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup> and plots of ECL emission and quenching data (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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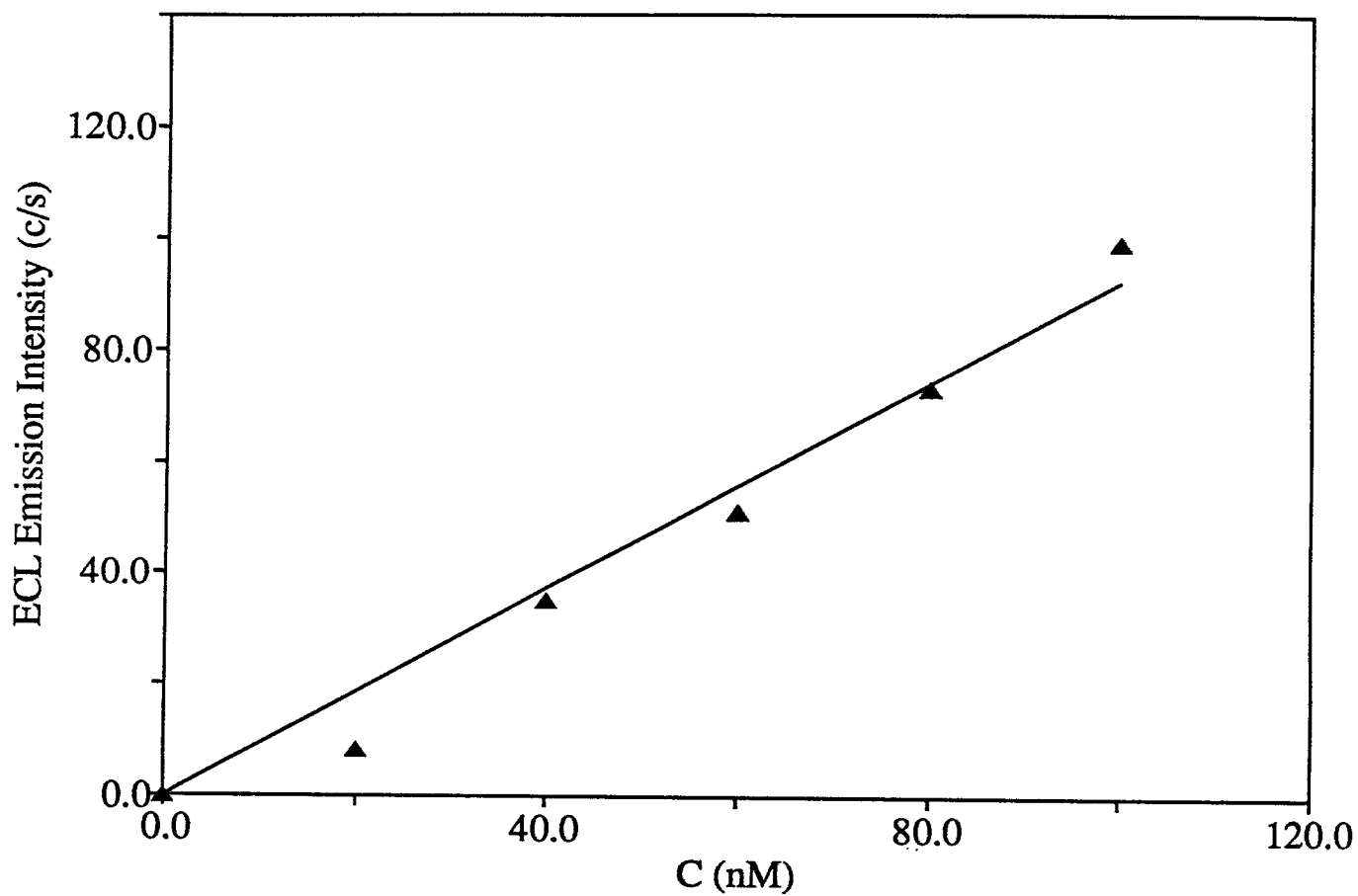
**Synthesis of Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup>.** Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded on a General Electric QE-300 NMR spectrometer using the residual peaks in the deuterated solvents as internal standards. Elemental analyses were performed by Atlantic Microlabs. Reverse phase chromatography was performed with a FPLC system (Pharmacia LKB) using a HR10/10 column packed with PepRPC 15 μm (C<sub>2</sub>/C<sub>18</sub>). The PF<sub>6</sub><sup>-</sup> salt of Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup> was prepared from the Cl<sup>-</sup> salt *via* precipitation from H<sub>2</sub>O with KPF<sub>6</sub>. The NO<sub>3</sub><sup>-</sup> salt of Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup> was prepared from the Cl<sup>-</sup> salt *via* anion exchange with KNO<sub>3</sub> using reverse phase chromatography.

**[Ru(1-(3-(4'-methyl-2,2'-bipyridin-4-yl)propyl)-1'-methyl-4,4'-bipyridinium)<sub>3</sub> (Ru<sup>II</sup>(MV<sup>2+</sup>-bpy)<sub>3</sub><sup>8+</sup>)·8Cl<sup>-</sup>·10H<sub>2</sub>O . [(1-(3-(4'-methyl-2,2'-bipyridin-4-yl)propyl)-1'-methyl-4,4'-bipyridinium)]<sup>1</sup>·Br<sup>-</sup>·I<sup>-</sup>** (93 mg, 0.16 mmol) and RuCl<sub>3</sub>·H<sub>2</sub>O (9 mg, 0.040 mmol) in 20% aqueous ethanol were heated at reflux for 12 hours under Ar. The solvent was removed using a rotary evaporator. The resulting red-orange solid was dissolved in 10 mL of a 50% saturated aqueous solution of KCl and loaded onto a reverse phase column. Reverse phase chromatography was performed using H<sub>2</sub>O as an elutant at a flow rate of 1.0 mL/min. The first band off the column was bright orange-red and eluted just ahead of a smaller red-orange band. The first band was collected and lyophilized. The resulting solid was resubjected to the same purification process and afforded 25 mg (37 %) of a bright orange-red solid. <sup>1</sup>H NMR (D<sub>2</sub>O) δ 2.4 (m, 15H, CH<sub>3</sub> and CH<sub>2</sub>), 2.87 (t, 6H, CH<sub>2</sub>), 4.41 (s, 9H, CH<sub>3</sub>), 4.73 (t, 6H, CH<sub>2</sub>), 7.09-9.08 (42H, m, aromatic H's); <sup>13</sup>C NMR (10 % CD<sub>3</sub>OD/D<sub>2</sub>O) δ 21.3, 31.8, 32.0, 62.3, 124.7, 124.7, 125.7, 125.8, 127.7, 128.0, 128.1, 129.1, 146.5, 147.3, 150.7, 151.1, 151.3, 151.4, 152.0, 152.0, 152.2, 157.3, 158.1; UV-Vis (H<sub>2</sub>O) λ<sub>max</sub> [nm] (ε): 258 (89 200), 284

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(107 000), 326 (12 000), 462 (14 800); Anal. Calcd. for  $C_{75}H_{78}N_{12}Ru \cdot 8Cl^- \cdot 10H_2O$ : C, 52.61; H, 5.77; N, 9.82; found: C, 52.87; H, 5.77; N, 9.70; FABMS ( $PF_6^-$  salt) *m/e* (relative intensity): 1827 (81), 1973 (100), 2116 (60).

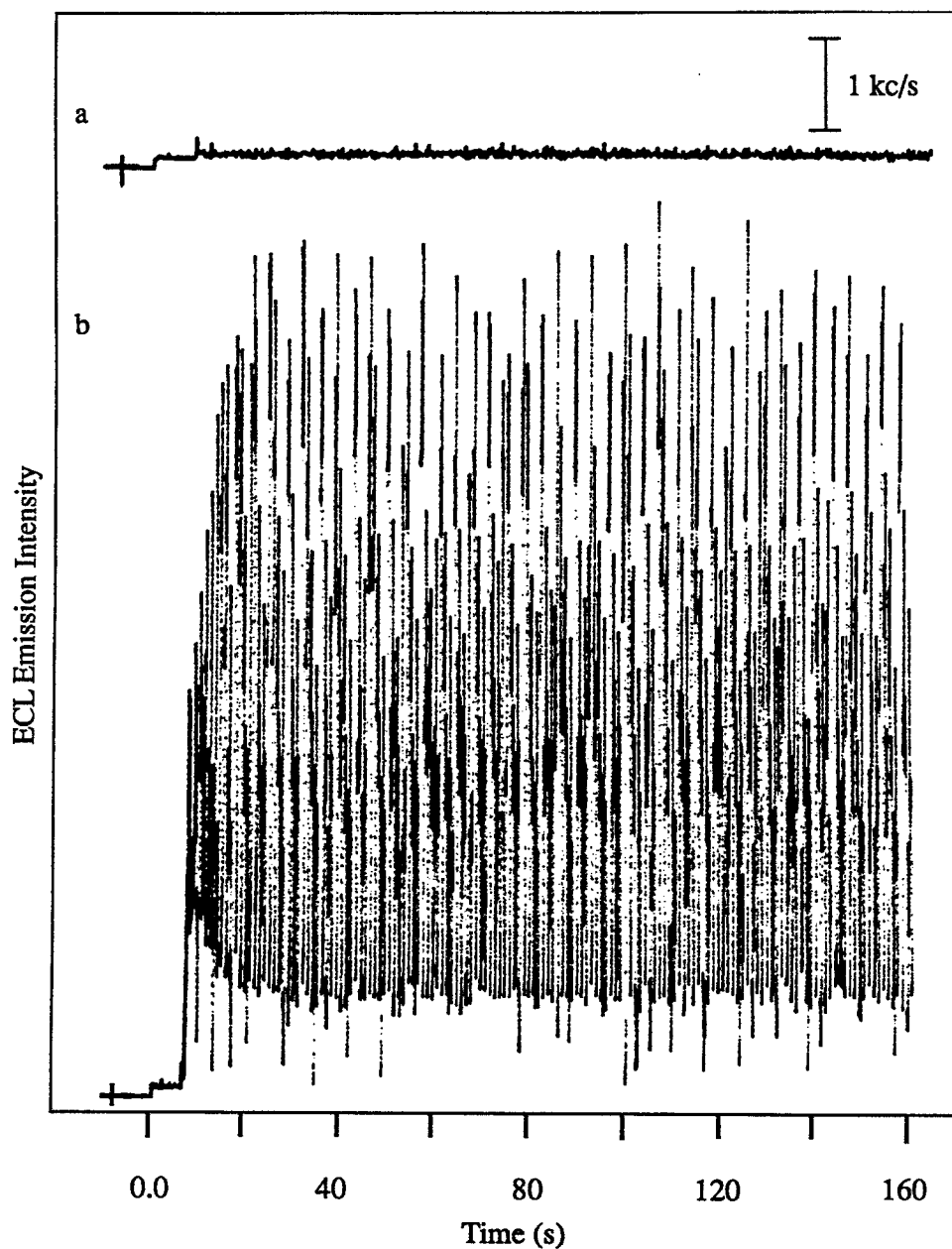
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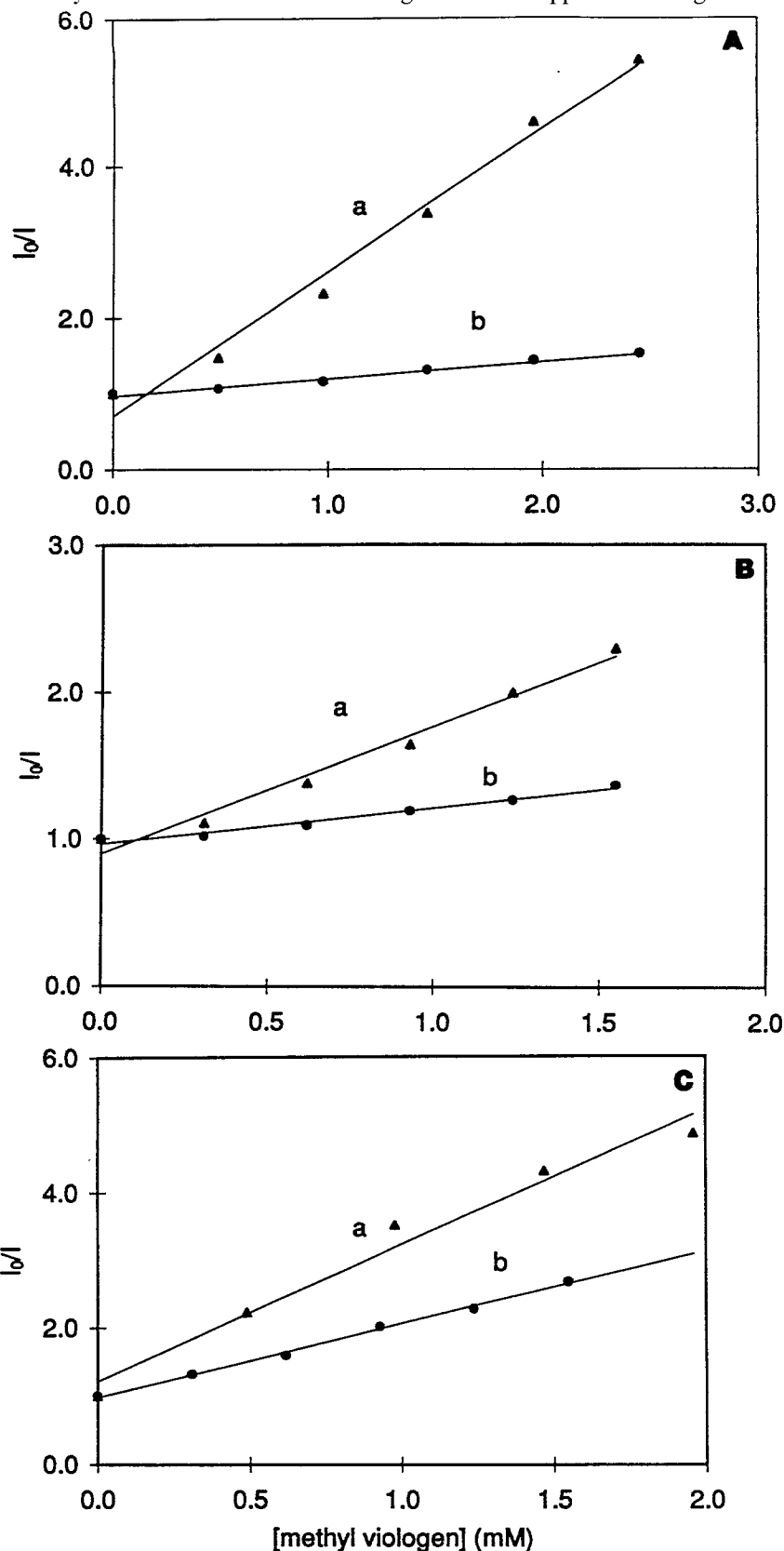
**Figure S1.** ECL peak emission of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  corrected for background from emission-potential transients like those in Figure 4b vs  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  concentration.



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**Figure S2.** ECL emission-time transients at a 0.071 cm<sup>2</sup> glassy carbon electrode in a 2.7 mM Ru<sup>II</sup>(bpy)<sub>2</sub>(MV<sup>2+</sup>-bpy)<sup>4+</sup> acetonitrile solution containing 0.2 M TBAPF<sub>6</sub> supporting electrolyte. Potentials were pulsed between (a) 1.60 and -0.2 V and (b) 1.60 and -0.60 V; pulse width, 0.2 s. Pulsing between 1.60 and -1.20 V produced results similar to b.



**Figure S3.** (A) Stern-Volmer plots of reciprocal normalized ECL and photoemission emission intensities of  $\text{Ru}(\text{bpy})_3^{2+}$  vs  $\text{MV}^{2+} \cdot 2\text{PF}_6^-$  concentration in 2 mM phosphate solution, pH 5, containing 25 mM  $\text{C}_2\text{O}_4^{2-}$ . (a) ECL peak emission resulting from transients like those in Figure 6. (b) Luminescence peak emission intensity. (B) As in (A) with 0.2 M phosphate buffer, pH 7.4, containing 0.15 M TPrA. (a) ECL peak emission. (b) Luminescence peak emission intensity. (C) Stern-Volmer plots of reciprocal normalized ECL intensity of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{MV}^{2+}\text{-bpy})^{4+}$  vs  $\text{MV}^{2+} \cdot 2\text{PF}_6^-$  concentration in (a) 2 mM phosphate buffer, pH 5, containing 25 mM  $\text{C}_2\text{O}_4^{2-}$  and (b) 0.2 M phosphate buffer, pH 7.4, containing 0.15 M TPrA.