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Electrogenerated Chemiluminescence. 62. Enhanced ECL in Bimetallic Assemblies with Ligands That Bridge Isolated Chromophores

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The electrogenerated chemiluminescence (ECL) of $[(bpy)_2Ru]_2(bphb)^{4+}$ (bphb = 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)benzene, bpy = 2,2′-bipyridine) and $(bpy)_2Ru(bphb)^{2+}$ in acetonitrile (MeCN), 50:50 (v/v) MeCN/H_2O, and aqueous solutions was studied. In both the mono- and bimetallic complexes, the ECL spectra are the same as the photoluminescence spectra, indicating the same metal-to-ligand charge-transfer states are formed in both ECL and photoluminescence. The bimetallic species produced more intense emission than $Ru(bpy)_3^{2+}$ in all solvent mixtures when ECL was generated via annihilation and with the coreactant tri-n-propylamine, which generates a strong reductant on oxidation. Relative ECL efficiencies for $[(bpy)_2Ru]_2(bphb)^{4+}$ were about 2–3 times that of $Ru(bpy)_3^{2+}$ in MeCN and aqueous media. ECL was also generated with the coreactant $S_2O_8^{2-}$, which produces the strong oxidant $SO_4^{\bullet-}$ upon reduction. However, the relative ECL efficiencies with $S_2O_8^{2-}$ were smaller (0.6–0.8) relative to the $Ru(bpy)_3^{2+}$. The monometallic species also displays ECL under the same conditions. However, the ECL intensity is dependent on both the solvent and the method of generating ECL. The mechanisms of ECL are discussed and digital simulation was employed to determine the most probable pathways for excited-state formation in the bimetallic species via the annihilation experiment. Because of their high ECL efficiencies, multimetallic systems of this type should be useful in the design of new labels for bioanalytical applications (e.g., immunoassays and DNA probes).

Following the discovery in 1959 by Paris and Brandt[1] that Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) is photoluminescent, a large body of literature has appeared aimed at understanding both the ground- and excited-state properties of Ru(bpy)$_3^{2+}$, Os(bpy)$_3^{2+}$, and their polyazine derivatives.[2,3] Fundamental and applied studies have followed, including the use of these complexes as sensitizers of photochemical electron transfer,[4,5] as building blocks for supramolecular arrays[5,6] in electron- and energy-transfer studies,[7] and as catalysts for small molecule activation.[8] These compounds have also played an important role in the development of electrogenerated chemiluminescence (ECL). ECL involves the formation of excited state species as a result of highly energetic electron-transfer reactions of reactants formed electrochemically. Several reviews have appeared on both the theory and application of ECL.[9–12] The first report of ECL in a metal chelate appeared in 1972, in which the excited state of Ru(bpy)$_3^{2+}$ was generated

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in nonaqueous media by electrochemical formation and subsequent annihilation of the reduced ($Ru(bpy)_3^+$) and oxidized ($Ru(bpy)_3^{3+}$) species.[13]

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^+ \qquad (1)$$

$$Ru(bpy)_3^{2+} - e^- \rightarrow Ru(bpy)_3^{3+} \qquad (2)$$

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^+ \rightarrow Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+*} \qquad (3)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \qquad (4)$$
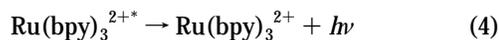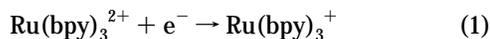
The potential range in nonaqueous solvents (e.g., +2.5 to −2.5 V vs NHE in MeCN) allows formation of the energetic precursors necessary in the annihilation sequence. However, given the limited potential window of water, alternative means must be used to produce the excited state (e.g., $Ru(bpy)_3^{2+*}$) for aqueous ECL. For example, in the presence of a luminophore such as $Ru(bpy)_3^{2+}$, oxidation of species like oxalate or tripropylamine (TPrA) or reduction of a species like peroxydisulfate ($S_2O_8^{2-}$) have been shown to generate the necessary energetic precursors for excited state formation.[11,12,14−17] The presumed mechanism involves formation of strong reductants ($CO_2^{\bullet-}$ or $TPrA^\bullet$) or strong oxidants ($SO_4^{\bullet-}$) that can interact with $Ru(bpy)_3^{3+}$ or $Ru(bpy)_3^+$, respectively, to produce the excited state:

$$Ru(bpy)_3^{3+} + TPrA^\bullet \rightarrow Ru(bpy)_3^{2+*} + products \qquad (5)$$

or

$$Ru(bpy)_3^+ + SO_4^{\bullet-} \rightarrow Ru(bpy)_3^{2+*} + SO_4^{2-} \qquad (6)$$
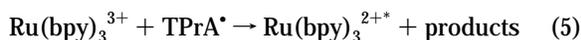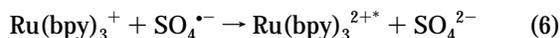
$Ru(bpy)_3^{2+}$ is used as an ECL-active label in DNA and immunoassay probes and for clinical analyses.[18] ECL has several advantages over other detection techniques like fluorescence because no excitation source is required, and thus, ECL is immune to interferences from luminescent impurities and scattered light. However, as with fluorescence labeling techniques, the sensitivity of the analysis depends on the ECL efficiency of the label.

With the goal of increasing the magnitude of ECL emission, this earlier work was extended to the use of multimetallic systems. Several reports on ECL with multimetallic systems have appeared, including Mo and W clusters[19,20] and a bimetallic Pt complex, Pt_2-(μ-$P_2O_5H_2$)$_4^{4-}$.[21,22] However, the ECL efficiency (taken as the number of photons emitted per redox event) in these systems was much weaker than $Ru(bpy)_3^{2+}$ under the same experimental conditions. Moreover, these earlier studies precluded the use of water because of the insolubility and instability of these complexes in an aqueous environment.[19−22] There have been no reports of ECL in multimetallic ruthenium systems. Often, coordination of a second metal center through a bridging-ligand (BL) framework (e.g., $L_2M(BL)ML_2$) leads to decreased photoluminescence quantum efficiencies and excited-state lifetimes. For example, $Ru(bpy)_3^{2+}$ has an excited-state lifetime of emission (τ_{em}) of ~600 ns[2,3] and an emission quantum efficiency (ϕ_{em}) in MeCN of 0.086.[23] Replacement of one bipyridine with a ligand capable of bridging two independent metal centers such as 2,3-bis(2′-pyridyl)pyrazine (dpp) results in a decrease of ϕ_{em} to 0.064 for $Ru(bpy)_2(dpp)^{2+}$ and $\tau_{em} \sim$ 200 ns.[24,25] Addition of a second $Ru(bpy)_2^{2+}$ moiety to form $[(bpy)_2Ru]_2(dpp)^{4+}$ gives $\phi_{em} = 0.0007$ and $\tau_{em} < 50$ ns.[24] This appears to be the general behavior. Other studies on Ru-(II) diimine systems have shown that the monometallic parent complex might be luminescent in fluid solution at room temperature, but the bimetallic system is usually not.[26] A number of these systems were prepared in mixed oxidation states (i.e., L_2M^{III}-(BL)$M^{II}L_2$) with the goal of defining the intervalence charge-transfer transition that is often present in the mixed-valence state.[27] In such studies, luminescence is not necessary to probe the photophysical and charge-transfer behavior. However, luminescence *is* a necessary prerequisite for efficient ECL.

The emission displayed by $[(bpy)_2Ru]_2(dpp)^{4+}$ and its monometallic analogue in fluid solution at room temperature has been traced to the weak metal−metal interaction present in the bimetallic system and the bipyridine-like environment conferred by the bridging dpp ligand.[24] However, even in this case, luminescence in the bimetallic system is much weaker than that observed in the parent compound. Many photophysical studies on ruthenium and osmium multimetallic complexes have centered on systems where the degree of electronic coupling between metal centers, as mediated by the BL-based orbitals, varies over orders of magnitude (i.e., Robin and Day class II and III systems).[26−29]

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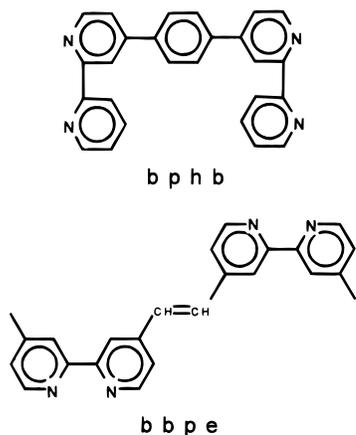
Figure 1. Structures of ligands: 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)benzene (bphb) and *trans*-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethene (bbpe).

In such systems, increased electronic coupling between metal centers is directly influenced by the energy and density of states of the BL. Increasing electronic density on the lowest-unoccupied π^* molecular orbitals and the acceptor orbitals active in the metal-to-ligand charge-transfer (MLCT) transitions that produce the excited state leads to enhanced communication. However, such systems rarely display high photoluminescence efficiencies. In fact, these systems rarely display any photoluminescence in fluid solution.[26] Despite the wealth of data on systems with significant interaction between metal centers, much less has been done on those where there is very weak coupling so that the metal centers are isolated or valence trapped (Robin and Day class I systems).[28,29]

In recent reports on bimetallic ruthenium systems with small electronic coupling between metal centers,[30–32] excited-state lifetimes that were greater than those for monometallic derivatives were reported. For example, $[(dmb)_2Ru]_2(bbpe)^{4+\ [31]}$ and $[(dmb)_2Ru]_2(bphb)^{4+\ [30]}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine, bbpe = *trans*-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethene, and bphb = 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)benzene, Figure 1) have τ_{em} = 1.31 and 1.57 μs, respectively, compared to 0.95 μs for the trissubstituted $Ru(dmb)_3^{2+}$ system. $(dmb)_2Ru(bphb)^{2+}$ yielded τ_{em} = 1.34 μs and ϕ_{em} = 0.109; ϕ_{em} for $[(dmb)_2Ru]_2(bphb)^{4+}$ was 0.125.[30] In contrast to previously studied systems, these bimetallic complexes clearly show increased efficiencies and lifetimes over the monometallic ones. This has been traced to a larger $Ru(d\pi) \rightarrow$ bphb (π^*) transition dipole and a smaller electron-vibrational coupling constant, resulting in a smaller degree of excited-state distortion.[30,31]

We report here efficient ECL in aqueous and nonaqueous fluid solution in $[(bpy)_2Ru]_2(bphb)^{4+}$ and in its monometallic analogue $(bpy)_2Ru(bphb)^{2+}$ using both annihilation and coreactant pathways. Digital simulation was used to determine the probable reaction sequences for formation of the excited states in the annihilation experiment, and the mechanism of ECL in such bimetallic assemblies is discussed. These studies expand upon earlier work on increasing the magnitude of ECL emission and extend the ECL methodology to multimetallic species for use in analytical applications.

EXPERIMENTAL SECTION

Materials. $(bpy)_2Ru(bphb)(PF_6)_2$ and $[(bpy)_2Ru]_2(bphb)-(PF_6)_4$ were available from previous studies.[30,32] These complexes were metathesized to the chloride salts for the aqueous experiments using tetra-*n*-butylammonium chloride (Bu$_4$NCl) dissolved in a minimal amount (<10 mL) of acetone. Tetra-*n*-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$, Sachem, Austin, TX) was used as the electrolyte and was recrystallized twice from 4:1 ethanol/water, dried in vacuo (110 °C), and stored in a vacuum desiccator before use. Tri-*n*-propylamine (TPrA, Aldrich) was used as received. MeCN was spectroquality (Burdick & Jackson) and stored over activated molecular sieves or in a Vacuum Atmosphere glovebox utilizing a He atmosphere. Deionized water from a Millipore Milli-Q system was used throughout. All other chemicals were reagent grade and used without further purification.

Methods. Cyclic voltammetric experiments without photon detection utilized a CH Instruments (Memphis, TN) Model 660 electrochemical work station. Cyclic voltammograms with photon detection employed a Princeton Applied Research 175 universal programmer (PAR, Princeton, NJ), a Model 173 potentiostat/galvanostat, and an Omnigraphic 2000 *x*−*y* recorder (Houston Instruments, Austin, TX).

A Model AT200 charge-coupled device (CCD) camera system (Photometrics, Ltd. Phoenix, AZ) cooled to −120 °C was used to acquire ECL spectra as well as to obtain integrated emission intensities used in the calculation of ECL efficiencies. A Chemspec 100S (American Holographic, Littleton, MA) spectrometer (focal length, 10 cm) was used to record ECL spectra. Light intensities were integrated for 10 min to record ECL emission spectra. Total integrated light intensities for efficiency measurements were obtained by focusing the lens of the CCD camera on the working electrode surface. Light intensities were then integrated for 5 min and the value reported represents an average over this time period. The CCD camera and the configuration of the experiment have been described in detail elsewhere.[16] Solutions used to obtain ECL spectra and emission intensities incorporated micromolar amounts of the Ru complex, 0.1 M Bu$_4$NPF$_6$, and 10 mM S$_2$O$_8^{2-}$ or 0.1 M TPrA.

Aqueous ECL efficiencies were determined using an Origen I electrochemiluminescent analyzer (Igen Inc., Rockville, MD). This system employs a flow injection cell, Au working and counter electrodes, and a Ag/AgCl gel reference electrode.[11] Photon detection utilized a photomultiplier tube directly above the working electrode. Stock solutions of each reagent (i.e., $(bpy)_2Ru(bphb)^{2+}$ and $[(bpy)_2Ru]_2(bphb)^{4+}$) and the $Ru(bpy)_3^{2+}$ standard were made by dissolving an appropriate amount of the chloride salt in a 100 mL sample of 0.2 M phosphate buffer solution (pH 7.5) containing TPrA. All subsequent solutions were made by diluting these stock solutions with buffer.

All nonaqueous and mixed-solvent (50:50 (v/v) MeCN/H$_2$O) experiments employed a conventional three-electrode configuration. The cell was designed to fit in front of the entrance slit to the CCD camera and had a total volume of 4−5 mL. A platinum

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disk electrode (0.2 cm diameter) sealed in glass was employed as the working electrode with a Pt wire auxiliary electrode and a silver wire quasi-reference electrode (AgQRE). Ferrocene was added as an internal reference and all potentials are reported relative to the NHE electrode (Fc/Fc$^+$ = 0.665 V vs NHE).[33]

The Pt working electrode was manually cleaned prior to each experiment by mechanical polishing on a felt pad (Buehler, Ltd., Lake Bluff, IL) with an aqueous slurry of 0.5 μm alumina (Buehler, Ltd.). The electrode was then rinsed with deionized water, immersed in concentrated nitric acid (~5 s), rinsed a second time, and then placed in a small beaker containing 95% EtOH followed by sonication for 5 min.

Solutions for ECL efficiency measurements were prepared in a drybox incorporating a He atmosphere or were prepared in air, purged with Ar, and then sealed in an air-tight cell. Before each ECL experiment, a cyclic voltammogram was recorded to establish the exact position of the redox processes vs the AgQRE. Digital simulations were performed using DigiSim 2.1 (Bioanalytical Systems, Inc.) interfaced with a PC.

Absorption spectra were recorded with an Aminco Bowman/Milton Roy Spectronic 3000 array spectrophotometer. Luminescence spectra were measured using an SLM Aminco SPF-500 spectrofluorometer. Relative photoluminescence quantum yields, ϕ_{em}, were measured in deaerated (Ar bubbled for 20 min) MeCN solutions at room temperature as reported previously[34] with Ru(bpy)$_3$(PF$_6$)$_2$ as the standard, ϕ_{em} = 0.086.[23]

RESULTS AND DISCUSSION

[(bpy)$_2$Ru]$_2$(bphb)$^{4+}$. Reductive and oxidative cyclic and square-wave votammograms are shown in Figures 2 and 3, respectively. The half-wave potentials ($E_{1/2}$) for oxidation and reduction of [(bpy)$_2$Ru]$_2$(bphb)$^{4+}$ are summarized in Table 1. Its first two one-electron reduction waves, separated by 150 mV,[32] are ligand-based with the first assigned to the electron localized on the BL.[30,32] The identity of the second wave is less clear, but by analogy to other Ru-based homobimetallics,[24,31,35] this reduction is probably also BL in nature.

$$[(bpy)_2Ru(bphb)Ru(bpy)_2]^{4+} + e^- \rightarrow$$
$$[(bpy)_2Ru(bphb^-)Ru(bpy)_2]^{3+} \quad (7)$$

$$[(bpy)_2Ru(bphb^-)Ru(bpy)_2]^{3+} + e^- \rightarrow$$
$$[(bpy)_2Ru(bphb^{2-})Ru(bpy)_2]^{2+} \quad (8)$$
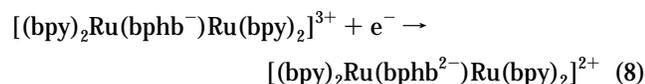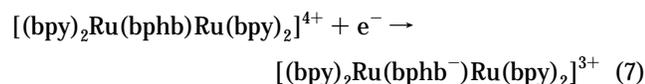
At more negative potentials a single, unresolved, two-electron wave appears (~−1.6 V) which, at a Pt electrode, displays a wave shape somewhat characteristic of an adsorptive process[36] with formation of neutral species. This suggests a two-electron reduction centered on the bpy ligands.

A single, unresolved, chemically reversible two-electron wave appears at +1.57 V for the Ru(II/III) couples (Figure 3).[30,32] The
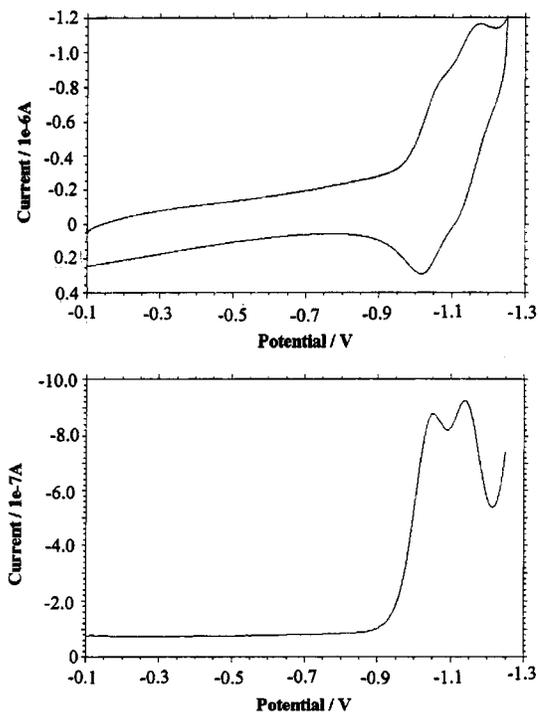
Figure 2. Reductive cyclic and square-wave voltammograms of 1 mM [(bpy)$_2$Ru]$_2$(bphb)(PF$_6$)$_4$ in MeCN/0.1 M Bu$_4$NPF$_6$. Scan rate 100 mV/s.
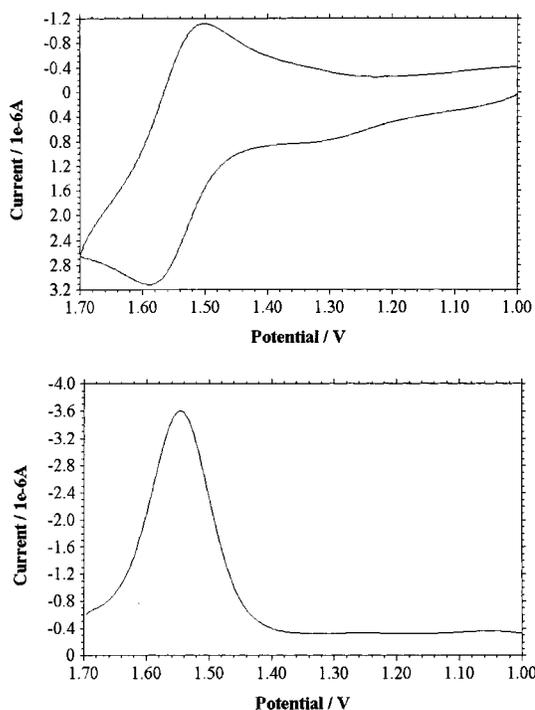
Figure 3. Oxidative cyclic and square-wave votammograms of [(bpy)$_2$Ru]$_2$(bphb)(PF$_6$)$_4$. Same conditions as in Figure 2.

absence of discrete oxidation waves, even in square-wave voltammetry, indicates that electronic coupling between the metal centers is small,[30,31] showing a system containing multiple non-interacting redox centers.[37] ECL was obtained during annihilation

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Table 1. Redox Potentials ($E°$)[a] for $(bpy)_2Ru(bphb)^{2+}$ and $[(bpy)_2Ru]_2(bphb)^{4+}$

	$E°$ (V vs NHE)[b]			
	oxidation	reductions		
complex				
$(bpy)_2Ru(bphb)^{2+}$	+1.569	−1.055	−1.235	−1.507
$[(bpy)_2Ru]_2(bphb)^{4+}$	+1.573	−1.051	−1.203	−1.575

[a] $E° = (E_{pa} + E_{pc})/2$. [b] Measured vs Fc/Fc$^+$ (+0.665 V vs NHE)[32] in MeCN/0.1 M (Bu$_4$N)$_2$PF$_6$.
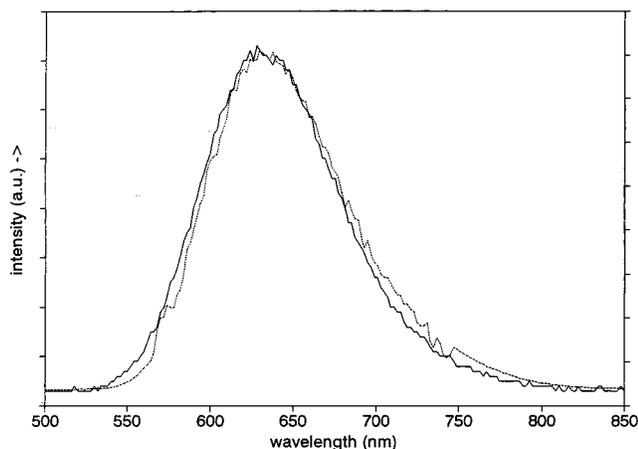
Figure 4. ECL emission spectra of 1 mM $[(bpy)_2Ru]_2(bphb)(PF_6)_4$ generated via annihilation (- - -) and in the presence of TPrA (—). MeCN solutions were 1 μM in complex, 0.1 M in TPrA, and 0.1 M in Bu$_4$-NPF$_6$, where appropriate. The annihilation spectrum was generated by alternate pulsing of the Pt electrode potential between +1.65 and −1.10 V. The TPrA spectrum was generated by pulsing of electrode potentials between 0 and +1.65 V via an oxidative−reductive coreactant sequence. Pulse length, 0.1 s. Annihilation spectrum (- - -) offset 5 nm to the red for clarity.

by first stepping to a potential corresponding to E_{pc}, the potential for the first BL-based reduction, and then to an E_{pa} corresponding to the formation of the Ru(II/III) couples. The ECL emission spectrum shown in Figure 4 is identical to that obtained with photoexcitation, indicating population of the same emitting (^{3}MLCT) states by the redox process as are formed photochemically. The ECL emission is clearly visible to the non-dark-adapted eye at millimolar concentrations, qualitatively indicating highly efficient ECL. For a more quantitative measure of relative efficiency, the area under the emission curve was integrated and compared to that of Ru(bpy)$_3^{2+}$ ($\phi_{ECL} \sim 0.05$)[38,39] under identical experimental conditions.[16,40] These results are shown in Table 2. The ECL quantum efficiency is defined as the number of photons emitted compared to the amount of reactant generated during a pulse (calculated from the integrated current).[16,40] In the bimetallic complex incorporating bphb, $\phi_{ECL} = 0.16 \pm 0.03$ is obtained for the annihilation in ECL, a value close to that predicted from the photoluminescence efficiencies in Table 2. This indicates that with $[(bpy)_2Ru]_2(bphb)^{4+}$, as with Ru(bpy)$_3^{2+}$ and related systems,[16,40] the overall yield of excited states formed during the annihilation reaction is close to unity.

Very intense ECL also results from the oxidation of MeCN and partially aqueous (50:50 (v/v) MeCN/H$_2$O) solutions containing $[(bpy)_2Ru]_2(bphb)^{4+}$ and TPrA (Figure 4) or reduction of mixtures of $[(bpy)_2Ru]_2(bphb)^{4+}$ and S$_2$O$_8^{2-}$. ECL was not observed under these conditions in solutions containing only $[(bpy)_2Ru]_2(bphb)^{4+}$ or only coreactant. Relative efficiencies, ϕ_r, are shown in Table 2. In experiments containing coreactants, the absolute ECL quantum efficiencies for the reference systems (i.e., Ru(bpy)$_3^{2+}$/TPrA and Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$) are unknown; thus relative efficiencies are reported taking that of Ru(bpy)$_3^{2+}$ as 1. In the $[(bpy)_2Ru]_2(bphb)^{4+}$/TPrA systems, the relative integrated ECL intensity is 2.5−3 times that of the corresponding Ru(bpy)$_3^{2+}$/ TPrA reference, i.e., about the same ratio as that observed in the $[(bpy)_2Ru]_2(bphb)^{4+}$ annihilation system. A partially aqueous environment did not perturb (i.e., decrease) the ECL intensity.

For the $[(bpy)_2Ru]_2(bphb)^{4+}$/S$_2$O$_8^{2-}$ systems, ϕ_{ECL} was only 0.6−0.8 times that of the Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ reference system, much less than that observed in the corresponding annihilation or TPrA sequences. The reasons for this are unclear. The MLCT states and hence luminescence in Ru(diimine) systems are sensitive to the nature of the coordination environment and the solvation shell.[2] ECL also depends on a number of factors, including electrolyte composition and concentration,[41] and the manner in which ECL is generated.[42] As with the $[(bpy)_2Ru]_2$-(bphb)$^{4+}$/TPrA system, ϕ_{ECL} does not appear to be greatly affected in a partially aqueous media.

Experiments were also performed in aqueous solutions of $[(bpy)_2Ru]_2(bphb)^{4+}$ and TPrA. The relative efficiencies were obtained by normalizing the relative intensities to concentration and are reported in Table 2. The value in the table is the average of at least six independent trials. While efficiencies in partially aqueous solution (50:50 (v/v) MeCN/H$_2$O) are comparable to those in MeCN, the efficiency is slightly lower in a purely aqueous environment ($\phi_{r,ECL} = 2$). The analyzer used for the aqueous experiments employs a flow injection cell for rapid and reproducible determinations of sequential samples.[17] Loss of luminophore by adsorption on the walls of both the tubing and cell can occur with polyaromatic hydrocarbons,[43] Ru(bpy)$_3^{2+}$, and related compounds.[16] Another possibility for loss in efficiency lies with the design of the electrochemical cell used in the Origen I analyzer. In the Origen I system,[17] the working and counter electrodes are in close proximity to one another, with the reference located downstream. This design results in a large iR drop across the cell, leading to uncertainty in the potential applied during the oxidative pulse sequence. If the potential is greater than that necessary to oxidize the metal centers, other processes (e.g., oxidation of solvent) can compete with the electron-transfer reactions necessary for ECL to occur. Despite the lower luminescence that occurs in an aqueous phosphate buffer medium, the factor of 2 increase over Ru(bpy)$_3^{2+}$ makes this system attractive as a label in aqueous ECL analyses. Even higher sensitivities should be possible with additional Ru centers linked to form the label. Note that the key issue is not efficiency per Ru

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Table 2. Spectroscopic and ECL Properties of (bpy)$_2$Ru(bphb)$^{2+}$ and [(bpy)$_2$Ru]$_2$(bphb)$^{4+}$

solvent[a]	λ_{em} (nm)	ϕ_{em}[b]	ϕ_{ann}[c]	$\phi_{r,TPrA}$[d]	$\phi_{r,Per}$[e]
		(bpy)$_2$Ru(bphb)$^{2+}$			
MeCN[f,g]	624	0.11 (±0.01)	0.0066 (±0.001)	1.5 (±0.3)	0.4 (±0.08)
MeCN/H$_2$O[h] (1:1 v/v)				1.6 (±0.3)	0.7 (± 0.1)
H$_2$O[i] (pH ~7)				0.058 (±0.01)	
		[(bpy)$_2$Ru]$_2$(bphb)$^{4+}$			
MeCN[f,g]	624[j]	0.158[j]	0.16 (±0.03)	2.6 (±0.5)	0.6 (±0.1)
MeCN/H$_2$O[h] (1:1 v/v)				2.8 (±0.6)	0.8 (±0.5)
H$_2$O[i] (pH ~7)				2.0 (± 0.4)	

[a] Micromolar solutions at 298 K degassed with Ar. [b] ϕ_{em} vs Ru(bpy)$_3^{2+}$ (0.086).[23] [c] ϕ_{ECL} vs Ru(bpy)$_3^{2+}$ (~0.05 for Ru(bpy)$_3^{2+}$). [d] Relative efficiency, [TPrA] = 0.15 M. [e] Relative efficiency, [S$_2$O$_8^{2-}$] = 10 mM. [f] Micromolar solutions at 298 K prepared in a glovebox with a He atmosphere. [g] 0.1 M Bu$_4$NPF$_6$ as electrolyte. [h] Bu$_4$NPF$_6$/Bu$_4$NClO$_4$ as electrolyte. [i] 0.2 M PO$_4^{3-}$ buffer (pH ~7) as supporting electrolyte. [j] Reference 32, recorded in MeCN at 298 K.
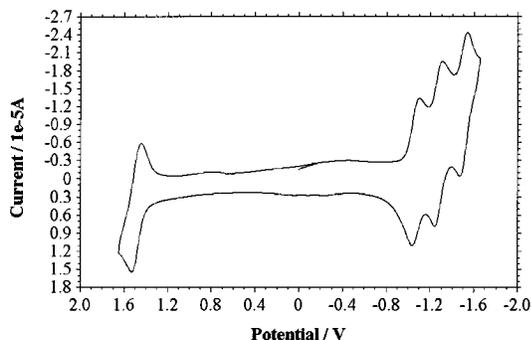
Figure 5. Cyclic voltammogram of (bpy)$_2$Ru(bphb)(PF$_6$)$_2$. Same conditions as in Figure 2.

Figure 6. ECL emission spectrum of (bpy)$_2$Ru(bphb)$^{2+}$ with (Bu$_4$N)-S$_2$O$_8$. MeCN solutions were 1 mM in complex, 10 mM in (Bu$_4$N)S$_2$O$_8$, and 0.1 M in Bu$_4$NPF$_6$. The S$_2$O$_8^{2-}$ spectra were generated by pulsing of the electrode potential between 0 and −1.1 V. Holding time at each limit was 0.1 s.

atom, but rather the total emission that can be generated from the label.

(bpy)$_2$Ru(bphb)$^{2+}$. Potentials for oxidation and reduction of (bpy)$_2$Ru(bphb)$^{2+}$ are listed in Table 1. The cyclic voltammogram in MeCN shown in Figure 5 is almost identical in appearance to that of Ru(bpy)$_3^{2+}$. All waves represent one-electron transfers, with the first reduction being BL in nature followed by sequential bpy-based reductions.[30]

$$(bpy)_2Ru^{II}(bphb)^{2+} + e^- \rightarrow (bpy)_2Ru^{II}(bphb^-)^{1+} \quad (9)$$

$$(bpy)_2Ru^{II}(bphb^-)^{1+} + e^- \rightarrow$$
$$(bpy^-)(bpy)Ru^{II}(bphb^-)^0 \quad (10)$$

$$(bpy^-)(bpy)Ru^{II}(bphb^-)^0 + e^- \rightarrow$$
$$(bpy^-)_2Ru^{II}(bphb^-)^{1-} \quad (11)$$
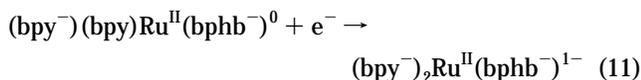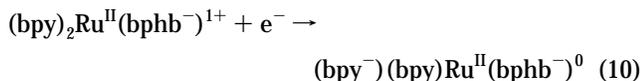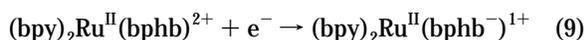
The lone oxidation has been assigned to the Ru(II/III) couple by comparison to (dmb)$_2$Ru(bphb)$^{2+}$.[30]

$$(bpy)_2Ru^{III}(bphb)^{3+} + e^- \rightarrow (bpy)_2Ru^{II}(bphb)^{2+} \quad (12)$$
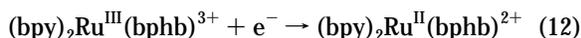
Bright orange ECL was obtained at the surface of the working electrode, as with the bimetallic system, utilizing both annihilation and coreactant methodology (Figure 6). Relative ECL efficiencies for the different pathways and in different solvent systems are reported in Table 2. (bpy)$_2$Ru(bphb)$^{2+}$ has a photoluminescence efficiency of 0.11 compared to Ru(bpy)$_3^{2+}$ (0.086).[23,30] This

compares quite well with the values obtained utilizing TPrA as a coreactant (ϕ_{ECL} = 1.5−1.6) in both MeCN and MeCN/H$_2$O. However, ECL efficiency in the annihilation experiment, (bpy)$_2$-Ru(bphb)$^{3+}$/(bpy)$_2$Ru(bphb)$^{1+}$ (ϕ_{ECL} = 0.007), was much smaller than for the Ru(bpy)$_3^{3+}$/Ru(bpy)$_3^{1+}$ reference system (ϕ_{ECL} = 0.05). This is unexpected considering the nature of the photoluminescence and the results obtained in the bimetallic complex. Similarly, aqueous ECL in 0.2 M phosphate buffer (pH 7.5) with TPrA as coreactant yielded efficiency values for (bpy)$_2$Ru(bphb)$^{2+}$ (ϕ_{ECL} = 0.058) much lower than the Ru(bpy)$_3^{2+}$ reference system ((ϕ_{ECL} = 1). These results reflect the sensitivity of the MLCT state to environment and the manner by which the excited state is formed. Moreover, in (bpy)$_2$Ru(bphb)$^{2+}$, only two of the four nitrogens in the BL are coordinated (i.e., one bpy arm in bphb, Figure 1), in contrast to [(bpy)$_2$Ru]$_2$(bphb)$^{4+}$ where both bpys in bphb are coordinated via the lone pairs on the N's. In the ECL experiment, the exposure of the free bpy in bphb may permit easier quenching, e.g., by excess reduced state, thereby decreasing luminescence. The ECL efficiencies for (bpy)$_2$Ru(bphb)$^{2+}$/TPrA in nonaqueous or partially aqueous media are higher where only the oxidized form is generated at the electrode.

As with [(bpy)$_2$Ru]$_2$(bphb)$^{4+}$, ϕ_{ECL} is less intense in (bpy)$_2$Ru-(bphb)$^{2+}$/S$_2$O$_8^{2-}$ than in Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$, despite the higher

photoluminescence of the former luminophore. This result may also reflect the unusually large intensity found with the Ru-$(bpy)_3^{2+}/S_2O_8^{2-}$ reference.[15,44] Under nonaqueous or partially aqueous conditions, $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ displays an overall higher ECL intensity than either $Ru(bpy)_3^{1+}/Ru(bpy)_3^{3+}$ or $Ru(bpy)_3^{2+}/$ TPrA under comparable experimental conditions.[44] The reasons for this are unclear, but for solutions of identical concentrations, both $[(bpy)_2Ru]_2(bphb)^{4+}$ and $(bpy)_2Ru(bphb)^{2+}$ with $S_2O_8^{2-}$ give intensities about the same as those incorporating TPrA.

In both TPrA and $S_2O_8^{2-}$, ϕ_{ECL} is not greatly affected by a partially aqueous medium and, within experimental error, may increase slightly upon addition of water. This probably reflects the hydrophobicity of diimine ligands and complexes and the ability of MeCN to form a protective shell around the luminophore.

Mechanism for $(bpy)_2Ru(bphb)^{2+}$. Mechanistically, ECL in the monometallic species appears to be analogous to Ru-$(bpy)_3^{2+}$.[13,15] Photochemically, excitation by a photon of light results in formation of a ^{1}MLCT state with the electron localized in the π^* orbitals of the BL. This is followed by intersystem crossing with subsequent formation of the triplet, ^{3}MLCT, state from which luminescence occurs. ECL generated by any of the methods discussed above produces spectra (e.g., Figure 6) identical to the photoluminescence. Therefore, the same orbitals are presumed to be responsible, whether the ^{3}MLCT state is formed electrochemically or photochemically. The energy of the emitting state (ΔH), as judged by the emission maximum, is 2.0 eV. From the standard potentials of the relevant half-reactions, a value of -2.6 eV is obtained corresponding to the total free energy (ΔG_{ann}) in the $(bpy)_2Ru(bphb)^{3+}$ $(-1.06$ V$)/(bpy)_2Ru(bphb)^{1+}$ (1.57 V) annihilation reaction.[9,10] Correcting for entropy ($T\Delta S \sim$ 0.1 eV) gives a corrected value for ΔH of 1.9 eV. For emission to occur by direct population of the emitting state, $\Delta G_{ann} > \Delta H - T\Delta S$ or $\Delta G_{ann} > \Delta H_{corr}$. Thus, the energy available in the annihilation sequence is well above that needed to form the ^{3}MLCT state, making this an energy sufficient system.[9,10]

By analogy to $Ru(bpy)_3^{2+}$ (eqs 1–4),[13–15] formation of $(bpy)_2$-$Ru(bphb)^{2+*}$ via annihilation can be explained by the following process, eqs 9 and 12 followed by

$$(bpy)_2Ru(bphb)^{1+} + (bpy)_2Ru(bphb)^{3+} \rightarrow$$
$$(bpy)_2Ru(bphb)^{2+*} + (bpy)_2Ru(bphb)^{2+} \quad (13)$$

$$(bpy)_2Ru(bphb)^{2+*} \rightarrow (bpy)_2Ru(bphb)^{2+} + h\nu \quad (14)$$
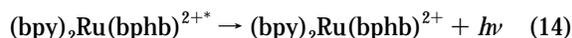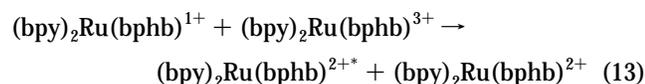
For solutions of $(bpy)_2Ru(bphb)^{2+}$ and $(Bu_4N)_2S_2O_8$, ECL was observed when the potential was swept negative enough to reduce the Ru system. Energetically, the relevant parameters in $(bpy)_2Ru$-$(bphb)^{2+}/S_2O_8^{2-}$ include ΔH_{corr} (1.9 eV), the same as in annihilation ECL, and the standard potentials for the pertinent reduction half-reactions:

$$SO_4^{\bullet-} + e^- = SO_4^{2-} \quad E^\circ = +3.0 \text{ V vs NHE}^{45} \quad (15)$$
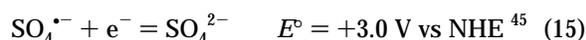
(44) Unpublished results from this laboratory.

and E° for the reduction of $(bpy)_2Ru(bphb)^{2+}$ (-1.05 V), eq 9, resulting in $\Delta G \sim -4.0$ eV. Clearly, the electron-transfer reaction between $(bpy)_2Ru(bphb)^{1+}$ and $SO_4^{\bullet-}$ is sufficient to produce triplet $(bpy)_2Ru(bphb)^{2+*}$ directly.

By analogy to $Ru(bpy)_3^{2+}$,[15] formation of $(bpy)_2Ru(bphb)^{2+*}$ occurs upon concomitant reduction of the luminophore and $S_2O_8^{2-}$, eqs 9 and 15 followed by

$$(bpy)_2Ru(bphb)^{1+} + SO_4^{\bullet-} \rightarrow$$
$$(bpy)_2Ru(bphb)^{2+*} + SO_4^{2-} \quad (16)$$
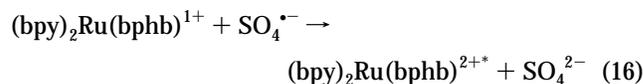
The source of $SO_4^{\bullet-}$ is thought to be the reaction

$$(bpy)_2Ru(bphb)^{1+} + S_2O_8^{2-} \rightarrow$$
$$(bpy)_2Ru(bphb)^{2+} + SO_4^{\bullet-} \quad (17)$$
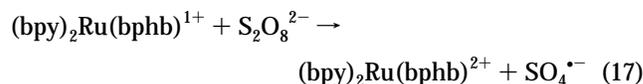
$SO_4^{\bullet-}$ can then react directly with the reduced luminophore to produce $(bpy)_2Ru(bphb)^{2+*}$, or as follows

$$(bpy)_2Ru(bphb)^{2+} + SO_4^{\bullet-} \rightarrow$$
$$(bpy)_2Ru(bphb)^{3+} + SO_4^{2-} \quad (18)$$
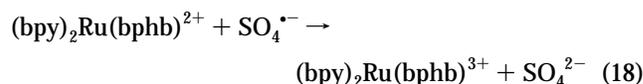
with excited-state formation occurring via annihilation (eqs 13 and 14).

In the TPrA reaction sequence, oxidation is believed to result in formation of a short-lived radical cation, which then loses a proton to form the strongly reducing intermediate $(CH_3CH_2$-$CH_2)_2N(C^\bullet HCH_2CH_3)$:[17,46]

$$TPrA - e^- \rightarrow TPrA^+ \rightarrow (CH_3CH_2CH_2)_2N(C^\bullet HCH_2CH_3) +$$
$$H^+ \quad E^\circ \sim 0.90 \text{ V vs NHE}^{43} \quad (19)$$

This radical is then available to react with the oxidized form of the luminophore, eq 12 followed by

$$(CH_3CH_2CH_2)_2N(C^\bullet HCH_2CH_3) + (bpy)_2Ru(bphb)^{3+} \rightarrow$$
$$(bpy)_2Ru(bphb)^{2+*} + products \quad (20)$$
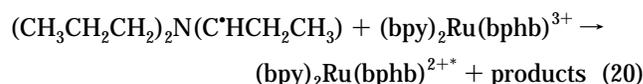
analogous to eq 5. Once again, the energetics of the electron-transfer reaction between $(bpy)_2Ru(bphb)^{3+}$ and the radical ($\Delta G \sim 2.5$ eV) is sufficient to directly produce the emitting ^{3}MLCT state.

Mechanism for $[(bpy)_2Ru]_2(bphb)^{4+}$. In considering the energetics of the ECL reactions in $[(bpy)_2Ru]_2(bphb)^{4+}$, one notes the similarity in the standard potentials for the relevant half-reactions (Table 1) and emission maxima (Table 2) with the monometallic parent compound. Thus, electron-transfer reactions in the $[(bpy)_2Ru]_2(bphb)^{6+}/[(bpy)_2Ru]_2(bphb)^{3+}$, $[(bpy)_2Ru]_2$-$(bphb)^{4+}/S_2O_8^{2-}$, and $[(bpy)_2Ru]_2(bphb)^{4+}/TPrA$ systems all have sufficient energy to produce directly the excited state.[9,10]

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Table 3

	oxidized forms		parent	reduced forms		excited state
charge	+6	+5	+4	+3	+2	(+4)*
symbol	C	B	A	D	E	L

Interaction between metal centers in $[(dmb)_2Ru]_2(bphb)^{4+}$ and the bpy derivative is small, as determined from cyclic voltammetric scans.[30] While this is one factor that results in enhanced photoluminescent and ECL efficiencies, it leads to complications in the interpretation of the ECL data because, electrochemically, oxidation of both metal centers occurs at nearly the same potential (i.e., with a statistical difference of 0.0356 V for noninteracting centers)[37] such that only a single unresolved two-electron wave appears in both cyclic and square-wave voltammetry (Figure 3). Similarly, the reduction waves are closely spaced, so that the direduced species is present during steps to negative potentials. The result is that, unlike the monomeric species $Ru(bpy)_3{}^{2+}$ and many other ECL-active species where only one-electron reduced and oxidized forms are produced, with the dimeric species two-electron oxidized and reduced forms are also produced at the electrode surface. However, as these diffuse toward the bulk solution they encounter parent species to produce the one-electron products in comproportionation reactions. The rates of these, as well as the electron-transfer reactions between oxidized and reduced species, are probably all near diffusion control. To obtain a qualitative picture of the concentration profiles that might exist during an annihilation experiment, digital simulations of the cyclic voltammetric experiments were carried out. Although the rate constants of the reactions are not known, the reactions are probably rapid, so all homogeneous electron-transfer reactions were assigned $k = 10^9$ M^{-1} s^{-1}. The different species are represented as in Table 3, and the luminescent decay of the excited state is not considered. Simulated voltammograms and concentration profiles of the different cases discussed are given in the Supporting Information. All assumed an initial concentration of A of 1 mM.

We consider first the oxidation reactions:

$$A - e \rightleftarrows B \qquad E^{\circ}_{54} = 1.57 \text{ V} \qquad (21)$$

$$B - e \rightleftarrows C \qquad E^{\circ}_{65} = 1.61 \text{ V} \qquad (22)$$

$$A + C \rightleftarrows 2B \qquad (23)$$
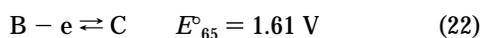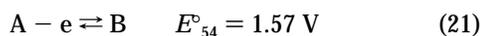
where E° for eq 22 is assumed to be 0.0356 V more positive than for eq 21[37] and the comproportionation reaction forms the mixed-valence state B, eq 23. Concentration (c) profiles as a function of distance from the electrode (x) show that as species C diffuses into bulk solution the comproportionation reaction with A produces a band of B.

For the reductive processes, the following equations apply:

$$A + e \rightleftarrows D \qquad E^{\circ}_{43} = -1.05 \text{ V} \qquad (24)$$

$$D + e \rightleftarrows E \qquad E^{\circ}_{32} = -1.20 \text{ V} \qquad (25)$$

$$A + E \rightleftarrows 2D \qquad (26)$$
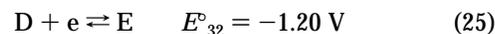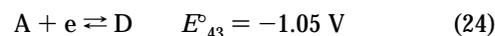
with the E°s determined experimentally. As with the oxidation, the comproportionation between E and A produces the one-electron reduced species D as E diffuses into solution.

To probe the homogenous electron-transfer reactions producing ECL in the annihilation sequence, the following reactions were incorporated into the simulation along with eqs 21−26 for potential sweeps at 1000 V/s from 0 to +2.0 to −1.5 V (encompassing the oxidation and reduction waves).

$$C + D \rightleftarrows B + L \qquad (27)$$

$$C + E \rightleftarrows A + L \qquad (28)$$

$$B + D \rightleftarrows A + L \qquad (29)$$

$$B + E \rightleftarrows L + D \qquad (30)$$

Reaction 28 presumes that a two-electron transfer can produce an excited state, which is unlikely. However, as shown below, its contribution to the overall emission process is minor. The simulations showed the buildup on L (its radiative and nonradiative conversion to A was neglected). By inclusion of all four reactions producing L, the concentration profile shows that a considerable amount of excited-state L is formed in the reactions following oxidation and reduction. However, elimination of eqs 27 and 28 in the reaction sequence showed that the amount of L was not greatly affected. In the absence of a quantitative reaction mechanism, details of the reactions producing the excited state cannot be obtained. However, the simulations suggest that the one-electron reactions (reduction of the +5 state, B, and oxidation of the +3 state, D) are the major contributors.

CONCLUSIONS

ECL occurs in the bimetallic system $[(bpy)_2Ru]_2(bphb)^{4+}$ and its monometallic parent $(bpy)_2Ru(bphb)^{2+}$ in MeCN and MeCN/H_2O via annihilation and with oxidative−reductive (TPrA) and reductive−oxidative ($S_2O_8{}^{2-}$) coreactants. The ECL emission with $[(bpy)_2Ru]_2(bphb)^{4+}$ in aqueous solution with the coreactant TPrA is twice that of $Ru(bpy)_3{}^{2+}$ at the same concentration, suggesting that it can improve the sensitivity in immunoassays and DNA probes by ECL. Even larger sensitivity improvements may be obtainable by linking additional Ru(II)(bpy)$_2$ units together via links where the centers do not interact.

Coordination of $(bpy)_2Ru^{2+}$ onto $(bpy)_2Ru(bphb)^{2+}$ leads to relative ECL efficiencies compared with $Ru(bpy)_3{}^{2+}$ close to those predicted from the photoluminescence efficiencies. These results indicate that formation of the lowest energy state responsible for luminescence, ^{3}MLCT, is close to unity. The intense emission observed in nonaqueous and partially aqueous solutions suggests that these types of multimetallic complexes might also be useful in ECL devices.

The ECL mechanism involves several possible reaction pathways, including annihilation and reaction with strong oxidants and strong reductants formed directly at the electrode or by homogenous electron-transfer reactions in solution.

ACKNOWLEDGMENT

SUPPORTING INFORMATION AVAILABLE

Simulated voltammograms and concentration profiles (9 pages). For ordering information and Internet access instructions see any current masthead page.