

Electrochemiluminescence of Ruthenium(II) Complexes Functionalized with Crown Ether Pendants and Effects of Cation Binding

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Electrochemiluminescence (ECL) of a series of ruthenium(II) diimine complexes with appended crown ethers derived from 1,10-phenanthroline was studied via either the annihilation route or the coreactant schemes, and the ECL efficiency has been determined. The effect of an FSN surfactant on the ECL properties was also studied in buffer solutions. The effect of cation binding on the ECL behavior was examined. The ECL intensity of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})](\text{ClO}_4)_2$ has been found to be strongly enhanced upon binding with Zn^{2+} and alkaline-earth metal ions. The X-ray crystal structure of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})](\text{ClO}_4)_2$ has also been determined.

Introduction

Electrochemiluminescence (ECL) of $[\text{Ru}(\text{bpy})_3]^{2+}$ has attracted much attention since the first report in 1972 by Bard's group¹ and has been widely used in chemical and biochemical analysis.² A major advantage of ECL over other detection techniques like fluorescence is that no excitation source is required, and thus the ECL method is immune to interferences from luminescent impurities and scattered light. $[\text{Ru}(\text{bpy})_3]^{2+}$ has become the most thoroughly studied ECL-active molecule because of its strong luminescence, good solubility in both aqueous and nonaqueous solutions, and ability to undergo reversible one-electron-transfer redox processes.³ In the first report of $[\text{Ru}(\text{bpy})_3]^{2+}$ ECL, the excited state was generated in aprotic media by annihilation of reduced and oxidized complex species.¹ Subsequently, ECL in an aqueous solution involving $[\text{Ru}(\text{bpy})_3]^{2+}$ and oxalate ($\text{C}_2\text{O}_4^{2-}$) was reported in 1981.⁴ Other species such as peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$)⁵ and tri-*n*-propylamine (TPRA)⁶

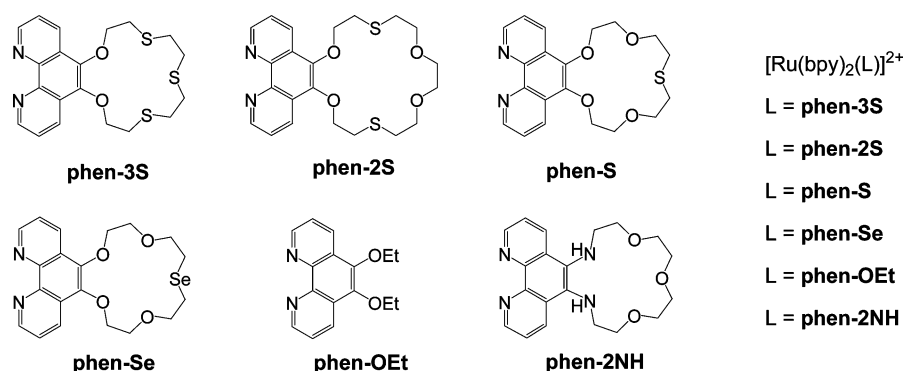
were also found to be able to serve as coreactants for $[\text{Ru}(\text{bpy})_3]^{2+}$ ECL. A number of $[\text{Ru}(\text{bpy})_3]^{2+}$ derivatives and other ruthenium(II) N,N-chelating complexes have been synthesized, and their ECL behaviors have been studied.⁷ These compounds generally display one-electron oxidation and reduction waves in their cyclic voltammograms, and strong ECL signals could be produced via a redox reaction of their oxidized and reduced forms (i.e., annihilation), identified as originating from the lowest triplet metal-to-ligand charge-transfer (³MLCT) state.⁸ Recently, the ECL study of ruthenium(II) complexes was extended to systems containing a crown ether (CE) moiety covalently bonded to a bipyridyl ligand. ECL of $[\text{Ru}(\text{bpy})_2(\text{AZA-bpy})]^{2+}$ [bpy = 2,2'-bipyridine; AZA-bpy = 4-(*N*-aza-18-crown-6-methyl-2,2'-bipyridine)]⁹ and $[\text{Ru}(\text{bpy})_2(\text{CE-bpy})]^{2+}$ [CE-bpy was a bipyridine ligand in which a CE (15-crown-5) was bound to the bpy ligand in the 3 and 3' positions]¹⁰ has been reported.

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Chart 1



It was found that the intensity of [Ru(bpy)₂(CE-bpy)]²⁺ ECL could be enhanced upon binding with Na⁺ ions in an aqueous buffer solution with TPrA as the coreactant. It has been suggested that the reaction of the CE moiety with Na⁺ might lead to a structural change of the complex that affected its luminescence and ECL efficiency. Similar effects of other metal ions on ECL of [Ru(bpy)₂(AZA-bpy)]²⁺ were also reported.⁹ All of these studies showed the versatility of ECL for sensing metal ions that were not directly involved in redox reactions. These tests would be useful for the determination of electrolytes and metal ions in clinical and environmental analysis. As an extension of our previous work on luminescent metal complexes containing oxa, thia, and seleno crown pendants,¹¹ herein is described ECL of the ruthenium(II) diimine complexes with appended CEs derived from 1,10-phenanthroline (Chart 1). The effects of metal ions on the ECL behavior of the ruthenium(II) complexes were also studied in acetonitrile solutions via the annihilation route or with (ⁿBu₄N)₂S₂O₈ as the coreactant.

Experimental Section

Tetra-*n*-butylammonium perchlorate, mercury(II) perchlorate hydrate, magnesium(II) perchlorate, calcium(II) perchlorate tetrahydrate, barium(II) perchlorate, cadmium(II) perchlorate hydrate, zinc(II) nitrate hydrate, and tri-*n*-propylamine were purchased from Aldrich Chemical Co., and the purity was over 99.0%. Zonyl FSN (40% fluorosurfactant, molecular formula F(CF₂CF₂)₃₋₈-CH₂CH₂O(CH₂CH₂O)_nH, 30% 2-propanol, and 30% H₂O) was purchased from Aldrich Chemical Co.. Tetra-*n*-butylammonium persulfate¹² was prepared according to the literature procedures,

and the ligands and ruthenium(II) complexes were synthesized according to that reported previously.^{11g}

The ECL spectra and ECL efficiency measurements were performed by using a CH Instruments, Inc., CHI 620 electrochemical analyzer. An Oriol InstaSpec V intensified charged-coupled device camera system (model 77195) cooled to -15 °C was used to acquire the ECL spectra as well as to obtain integrated emission intensities used in the calculation of ECL efficiencies. Light intensities were integrated over 2 min in the acquisition of the ECL spectra. A square Pt net (0.64 cm²) was employed as the working electrode. The reference electrode was a Ag wire, while a Pt wire was used as the counter electrode. The ECL emission efficiency was defined as the number of photons generated from an electrochemical event.¹³ Solutions for ECL studies contained complexes in millimolar concentration.

In the study of the effect of a nonionic surfactant on ECL, the measurements were performed on a CH Instruments, Inc., CHI 600A electrochemical workstation. A 2-mm-diameter Au electrode (CH Instruments, Inc.) was employed as the working electrode. The reference electrode was a saturated calomel electrode (SCE), and a Pt wire was used as the counter electrode. Before each experiment, the Au working electrode was subjected to repeated scanning in the potential range of -0.5 to +1.4 V (vs SCE) in a phosphate buffer (0.1 M) until reproducible voltammograms were obtained and was then rinsed with Milli-Q water. The ECL signals along with the cyclic voltammograms were measured with a photomultiplier tube (PMT; Hamamatsu R928) installed under the electrochemical cell. A voltage of -800 V was supplied to the PMT with the Sciencetech PMH-02 (Sciencetech Inc., Hamilton, Ontario, Canada) high-voltage supply. Solutions used to obtain the ECL signals in the presence of fluorosurfactants contained the ruthenium(II) complex in micromolar concentration and TPrA (0.1 M) in a phosphate buffer (0.1 M, pH = 7.5).

For a cation-binding study, the instrument was the same as that described above for the study of the nonionic surfactant effect except that a 2-mm-diameter glassy carbon electrode (CH Instruments, Inc.) was employed in place of the Au electrode as the working electrode and the reference electrode was a Ag/AgCl electrode. The glassy carbon electrode was treated prior to use by polishing with 0.3 μm α-alumina (Linde), followed by rinsing with ultrapure (18 MΩ) deionized water and sonication for about 1 min, and then finally rinsed under a stream of ultrapure deionized water and high-performance liquid chromatography acetonitrile. Solutions used to obtain the ECL signals contained a micromolar amount of the

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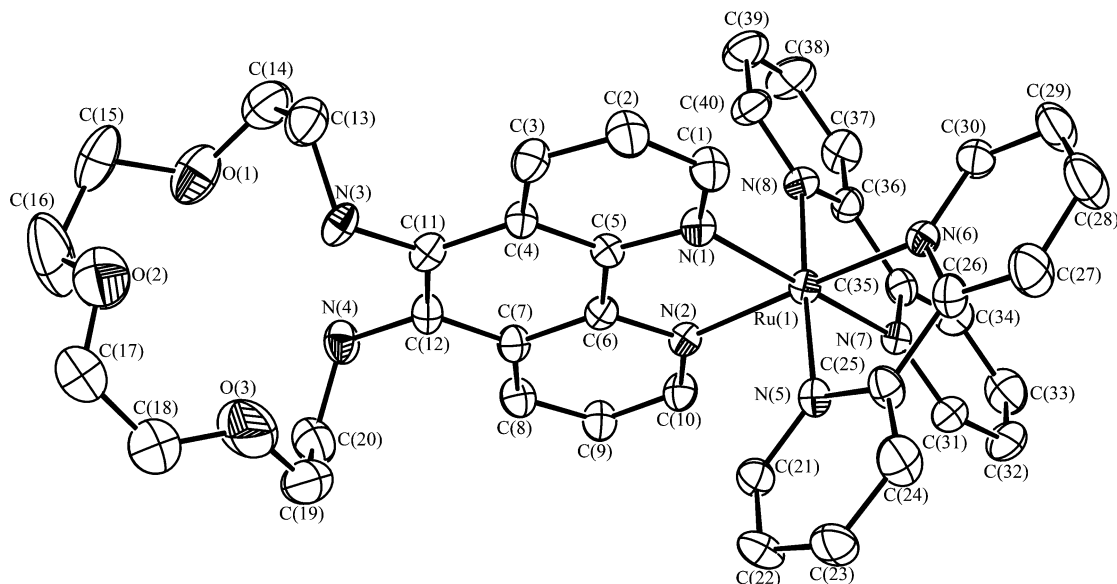


Figure 1. Perspective drawing of the complex cation of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})](\text{ClO}_4)_2$ with atomic numbering. H atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

ruthenium(II) complex, with $n\text{Bu}_4\text{NClO}_4$ (0.1 M) and $\text{S}_2\text{O}_8^{2-}$ (2 mM) in nonaqueous acetonitrile.

X-ray Crystallography. Crystal data for $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})](\text{ClO}_4)_2 \cdot 0.75\text{CH}_3\text{CN} \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$: $[\text{C}_{42}\text{H}_{44.25}\text{Cl}_3\text{N}_{8.75}\text{O}_{11.50}\text{Ru}]$, fw = 1063.02, orthorhombic, $Pnmm$, $a = 30.258(6)$ Å, $b = 15.656(3)$ Å, $c = 20.218(4)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 9578(3)$ Å³, $Z = 8$, $D_c = 1.474$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 0.562$ mm⁻¹, $F(000) = 4340$, and $T = 301$ K. A crystal of dimensions 0.4 mm \times 0.4 mm \times 0.1 mm mounted in a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Data collection was made with a 2° oscillation step of φ , 600 s of exposure time, and a scanner distance at 120 mm. A total of 100 images were collected and interpreted, and intensities were integrated using the program *DENZO*.¹⁴ The structure of the complex was solved by direct methods employing the *SIR-97* program¹⁵ on a PC, and Ru and many non-H atoms were located according to the direct methods and the successive least-squares Fourier cycles. The positions of other non-H atoms were found after successful refinement by full-matrix least squares using the program *SHELXL-97*¹⁶ on a PC. The positions of the H atoms were calculated based on the riding mode, with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of the final R indices. A total of 28 802 reflections were measured, including 7634 unique ($R_{\text{int}} = 0.0705$) reflections of which 3979 [$I > 2\sigma(I)$] reflections were used for refinement with $R1 = 0.0655$ and $wR2 = 0.1881$ with a goodness of fit of 0.951.

Results and Discussion

Crystal Structure Determination. Crystal structures of the complexes $[\text{Ru}(\text{bpy})_2(\text{phen-3S})](\text{ClO}_4)_2$, $[\text{Ru}(\text{bpy})_2(\text{phen-2S})](\text{ClO}_4)_2$, $[\text{Ru}(\text{bpy})_2(\text{phen-S})](\text{ClO}_4)_2$, and $[\text{Ru}(\text{bpy})_2(\text{phen-Se})](\text{ClO}_4)_2$ were determined in an earlier report.^{11g} Single crystals of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})](\text{ClO}_4)_2$ were obtained by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. The perspective drawing of the complex cation is depicted in Figure 1. The Ru atom adopted a distorted octahedral geometry, with the angle subtended by the N atoms of the phenanthroline ligand at the Ru center of $79.5(2)^\circ$, which is much smaller than the ideal angle of 90° adopted in the octahedral geometry. The deviation from the ideal angle was ascribed to the steric requirement of the chelating ligands, which was commonly observed in other related complex systems.¹⁷ The bond distances of Ru(1)–N(1) and Ru(1)–N(2) were 2.067(5) and 2.063(5) Å, respectively, which were typical of those found in other ruthenium(II) polypyridyl complexes.^{11g,17,18} The N atoms [N(3) and N(4)] on the crown unit were found to lie on the same plane as the phenanthroline ring, and the angles of N(3)–C(11)–C(4) and N(4)–C(12)–C(7) were $118.3(7)^\circ$ and $118.0(7)^\circ$, respectively, which were close to the ideal angle of 120° adopted in the geometry of sp² hybridization of carbon. The torsion angles of C(13)–N(3)–C(11)–C(4) and C(20)–N(4)–C(12)–C(7) were 75.963° and 73.165° , respectively.

ECL Quantum Efficiency. These ruthenium(II) diimine complexes with appended CEs derived from 1,10-phenanthroline showed redox properties typical of that of ruthenium(II) polypyridine derivatives,¹⁹ and the replacement of a different substituted 1,10-phenanthroline CE ligand did not cause a significant influence on the redox behavior.^{11g} Because ECL of ruthenium(II) chelate could be generated

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Table 1. ECL and Emission Quantum Efficiency of the Ruthenium(II) Complexes

complex	ϕ_{em}^a	ϕ_{ECL}			
		ϕ^b	ϕ^c	ϕ^d	ϕ^e
[Ru(bpy) ₂ (phen-3S)](ClO ₄) ₂	0.058	<i>f</i>	0.51	0.43	0.57
[Ru(bpy) ₂ (phen-2S)](ClO ₄) ₂	0.060	<i>f</i>	0.76	0.67	0.73
[Ru(bpy) ₂ (phen-S)](ClO ₄) ₂	0.060	0.048	1.26	0.96	0.90
[Ru(bpy) ₂ (phen-Se)](ClO ₄) ₂	0.063	0.070	0.87	0.94	1.07
[Ru(bpy) ₂ (phen-OEt)](ClO ₄) ₂	0.064	0.065	1.36	1.83	1.54
[Ru(bpy) ₂ (phen-2NH)](ClO ₄) ₂	0.014	<i>f</i>	0.35	0.36	0.40

^a Emission quantum efficiency in degassed CH₃CN. From ref 11g. ^b ϕ_{ECL} vs [Ru(bpy)₃]²⁺ (0.05)¹³ in nonaqueous CH₃CN by the annihilation method. ^c Relative ECL efficiency vs [Ru(bpy)₃]²⁺ (1.0) and TPrA (0.1 M) in a phosphate buffer (0.1 M, pH = 7.5). ^d Relative ECL efficiency vs [Ru(bpy)₃]²⁺ (1.0), containing ⁿBu₄NClO₄ (0.1 M) and S₂O₈²⁻ (5 mM) in a CH₃CN–H₂O mixture (9:1, v/v). ^e Relative ECL efficiency vs [Ru(bpy)₃]²⁺ (1.0), containing ⁿBu₄NClO₄ (0.1 M) and S₂O₈²⁻ (5 mM) in nonaqueous CH₃CN. ^f ECL signals were too weak to allow an accurate measurement.

by applying different electrochemical excitations, three reaction schemes, i.e., annihilation,¹ oxidative reduction,⁴ and reductive oxidation,⁵ were used to produce the luminescent excited state, i.e., the MLCT emissive state. The ECL efficiency in each reaction route has been determined by using [Ru(bpy)₃]²⁺ as the standard. The results are shown in Table 1. The photoluminescence quantum yields of the complexes were also included for comparison. The ECL spectra were identical with those of photoluminescence, indicating that the same emitting (³MLCT) states were responsible for the ECL emission of these complexes.

The annihilation ECL signals were generated by alternate pulsing of the electrode potential to form the oxidized and reduced complex species in acetonitrile solutions. The ECL quantum efficiency of [Ru(bpy)₂(**phen-S**)]²⁺ was found to be similar to that of [Ru(bpy)₃]²⁺ ($\phi_{ECL} \sim 0.05$).¹³ For [Ru(bpy)₂(**phen-Se**)]²⁺ ($\phi_{ECL} \sim 0.070$) and [Ru(bpy)₂(**phen-OEt**)]²⁺ ($\phi_{ECL} \sim 0.065$), the ϕ_{ECL} values were slightly larger than that of [Ru(bpy)₃]²⁺, in agreement with their higher photoluminescence efficiencies.^{11g} However, the ECL signals of [Ru(bpy)₂(**phen-3S**)]²⁺, [Ru(bpy)₂(**phen-2S**)]²⁺, and [Ru(bpy)₂(**phen-NH**)]²⁺ were too weak to allow an accurate measurement of their ECL efficiencies in our studied system because the ratio of signal-to-noise was smaller than 3.

The oxidative-reduction ECL studies were conducted in phosphate buffer solutions (0.1 M, pH = 7.5), and TPrA (0.1 M) was used as the coreactant. The ECL signals were produced upon concomitant oxidation of the complexes and TPrA. According to earlier reports,²⁰ TPrA oxidation would lead to the formation of a short-lived TPrA radical cation, which was believed to lose a proton from the α -carbon to form a strongly reducing intermediate, TPrA^{*}, which then reduced [Ru(bpy)₃]³⁺ to generate the excited state [Ru(bpy)₃]^{2+*}. Following similar mechanisms, the complexes

showed relative ECL efficiencies in the order [Ru(bpy)₂(**phen-OEt**)]²⁺ (1.36) > [Ru(bpy)₂(**phen-S**)]²⁺ (1.26) > [Ru(bpy)₂(**phen-Se**)]²⁺ (0.87) > [Ru(bpy)₂(**phen-2S**)]²⁺ (0.76) > [Ru(bpy)₂(**phen-3S**)]²⁺ (0.51) > [Ru(bpy)₂(**phen-2NH**)]²⁺ (0.35). Except for [Ru(bpy)₂(**phen-S**)]²⁺ and [Ru(bpy)₂(**phen-Se**)]²⁺, the trend was the same as that of the photoluminescence efficiency.

In the reductive-oxidation ECL reactions, S₂O₈²⁻ (5 mM) was used as the coreactant in nonaqueous acetonitrile or a acetonitrile–H₂O (9:1, v/v) mixture containing ⁿBu₄NClO₄ (0.1 M) as the supporting electrolyte. Persulfate was reduced to the strong oxidant SO₄^{•-}, which then underwent an electron-transfer reaction with the reduced ECL luminophore to generate light.⁵ The relative ECL efficiency attained in the acetonitrile–H₂O mixture followed the order of [Ru(bpy)₂(**phen-OEt**)]²⁺ (1.83) > [Ru(bpy)₂(**phen-Se**)]²⁺ (0.94) \approx [Ru(bpy)₂(**phen-S**)]²⁺ (0.96) > [Ru(bpy)₂(**phen-2S**)]²⁺ (0.67) > [Ru(bpy)₂(**phen-3S**)]²⁺ (0.43) > [Ru(bpy)₂(**phen-2NH**)]²⁺ (0.36). In the nonaqueous acetonitrile solution, the ECL efficiency was found to be in the sequence of [Ru(bpy)₂(**phen-OEt**)]²⁺ (1.54) > [Ru(bpy)₂(**phen-Se**)]²⁺ (1.07) > [Ru(bpy)₂(**phen-S**)]²⁺ (0.9) > [Ru(bpy)₂(**phen-2S**)]²⁺ (0.73) > [Ru(bpy)₂(**phen-3S**)]²⁺ (0.57) > [Ru(bpy)₂(**phen-2NH**)]²⁺ (0.4). Although there was a slight discrepancy between the orders of ECL and photoluminescence efficiency, a relationship between them could be established from these results. In general, the greater the number of electron-rich soft donor atoms on the CE and the stronger the electron-donating ability of the crown ligand, the weaker would be the ECL and photoluminescence efficiency of the ruthenium(II) polypyridine complexes. Among the complexes, [Ru(bpy)₂(**phen-2NH**)]²⁺ showed the lowest luminescence quantum yield and ECL efficiency, which could probably be attributable to the electron-donating ability of the diaza group on the crown. Because the diaza groups were directly coordinated to the phenanthroline unit, they would exhibit the strongest electron-donating effect, which led to electron-transfer quenching of the emissive ³MLCT state.

Effect of a Nonionic Fluorosurfactant on ECL of a Ruthenium(II) Complex/TPrA System. The effects of surfactants on the ECL of the [Ru(bpy)₃]²⁺/TPrA system have been of interest.²¹ Recent reports demonstrated that the nonionic fluorosurfactant (Zonyl FSN) could strongly enhance the ECL intensity of the [Ru(bpy)₃]²⁺/TPrA system at a Au electrode. The FSN adsorption layer not only rendered the electrode surface more hydrophobic but also effectively suppressed the growth of electrode oxides in the potential region less positive than +1.0 V vs SCE, leading to more facile oxidation of TPrA and an intense low-oxidation-potential (LOP) ECL signal.²² LOP ECL was produced at potentials well before the oxidation of [Ru(bpy)₃]²⁺ via a novel mechanism involving the intermediacy

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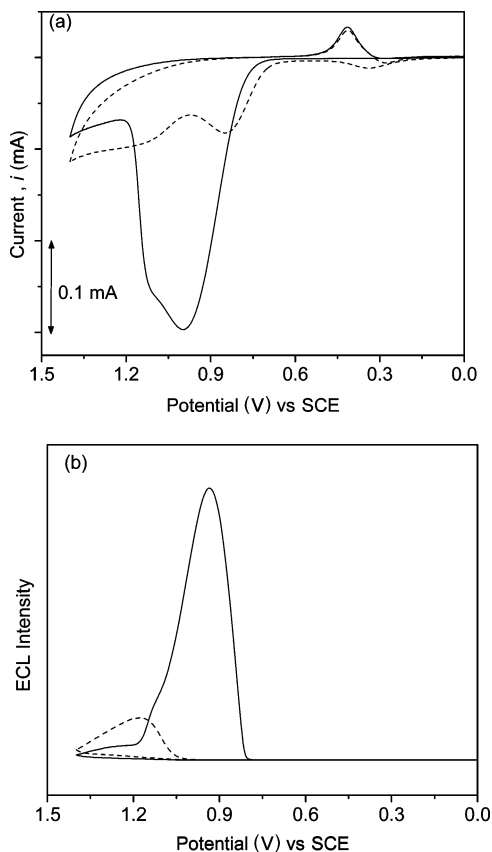


Figure 2. Cyclic voltammograms (a) and corresponding ECL signals (b) for $[\text{Ru}(\text{bpy})_2(\text{phen-3S})]^{2+}$ ($1 \mu\text{M}$), 0.1 M TPrA, and 0.1 M phosphate buffer ($\text{pH} = 7.5$) in the absence (---) and presence (—) of FSN on the Au electrode surface. Scan rate: 100 mV s^{-1} .

of TPrA cation radicals in the generation of $[\text{Ru}(\text{bpy})_3]^{2+*}$.²³ Up to now, only $[\text{Ru}(\text{bpy})_3]^{2+}$ and its derivatives have been found to be able to produce ECL following the LOP emission route. In this study, we examined the fluorosurfactant effect on ECL of the new complexes $[\text{Ru}(\text{bpy})_2(\text{phen-3S})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ with TPrA as the coreactant in a phosphate buffer at a Au electrode and revealed that ECL of these complexes could also be produced efficiently via the LOP ECL scheme.

Figure 2 shows that, in the absence of the surfactant species, the cyclic voltammogram and the ECL signal of $[\text{Ru}(\text{bpy})_2(\text{phen-3S})]^{2+}$ /TPrA system at a Au electrode were similar to those of $[\text{Ru}(\text{bpy})_3]^{2+}$ /TPrA reported previously (note that the anodic current mainly resulted from the oxidation of TPrA because of the low concentration of the ruthenium(II) complex and the ECL signal of TPrA in a phosphate buffer was not observable).²² TPrA started to be oxidized at $+0.85 \text{ V}$, and the ECL peak appeared at $+1.18 \text{ V}$. After the electrode was pretreated in an aqueous solution of FSN ($0.1 \text{ wt } \%$) for 5 min , a much larger TPrA oxidation current was observed in the potential region between $+0.8$ and $+1.2 \text{ V}$. Simultaneously, a new intense ECL peak appeared at $+0.92 \text{ V}$ and its maximum intensity was about 8 times larger than that obtained at $+1.18 \text{ V}$ at the surfactant-free electrode. Similar results were observed for $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$. The mechanism of the LOP ECL of

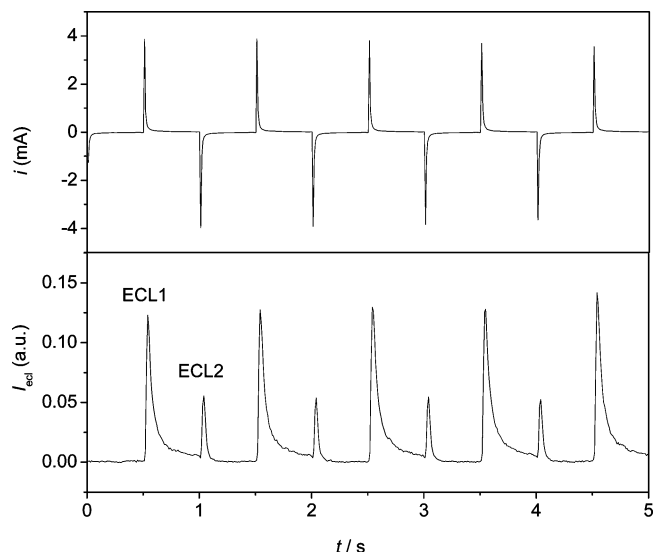
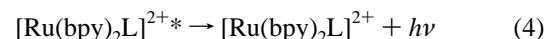
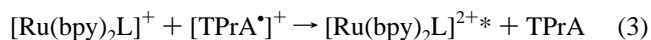
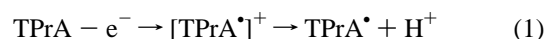


Figure 3. Chronoamperometric transient and corresponding ECL curve for $200 \mu\text{M}$ $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ in an acetonitrile solution containing 0.1 M $n\text{Bu}_4\text{NClO}_4$. Working electrode: glassy carbon. The chronoamperometry settings are as follows: initial potential, 0 V ; upper limit of the potential scan, $+1.5 \text{ V}$; lower limit of the potential scan, -1.5 V ; initial step direction, positive; potential pulse width, 0.5 s .

$[\text{Ru}(\text{bpy})_2(\text{phen-3S})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ could be similar to that of the $[\text{Ru}(\text{bpy})_3]^{2+}$ /TPrA system:



In this route, only TPrA was oxidized on the electrode while the oxidation of $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ was not required.

Cation-Binding Studies. Our previous study revealed that the binding of metal ions to $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ could cause a strong enhancement in the emission intensities of the complex, and the binding constants (K_s) of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ to Mg^{2+} , Ca^{2+} , Ba^{2+} , and Zn^{2+} were in the order of ca. $10^4 \text{ dm}^3 \text{ mol}^{-1}$.^{11g} In this study, the cation-binding property of the complex has been probed using ECL. Annihilation ECL signals of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ ($200 \mu\text{M}$) in an acetonitrile solution containing 0.1 M $n\text{Bu}_4\text{NClO}_4$ as the supporting electrolyte are shown in Figure 3. The intensities of the ECL signals during the negative potential pulse (ECL1) and positive potential pulse (ECL2) were different, which could be attributed to the difference in stability of the cation radicals and the anion radicals of the complex. The lower intensity of ECL2 suggested the shorter lifetime of the anion radicals. The time course of the annihilation ECL signals upon the addition of Ca^{2+} ions is shown in Figure 4. The ECL signals showed a slight drop in intensity immediately after Ca^{2+} was injected because of the disturbance of the solution; a similar phenomenon was observed when a blank solution was injected. After a reaction time of about 20 s , the effect of cation binding resulted in obvious intensity enhancement of both ECL1 and ECL2

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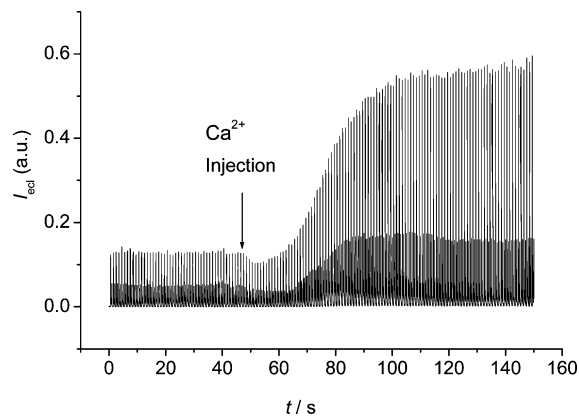


Figure 4. Time course of the annihilation ECL signals of 200 μM $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ upon the addition of 1 mM $\text{Ca}(\text{ClO}_4)_2$. Conditions were the same as those employed in Figure 3.

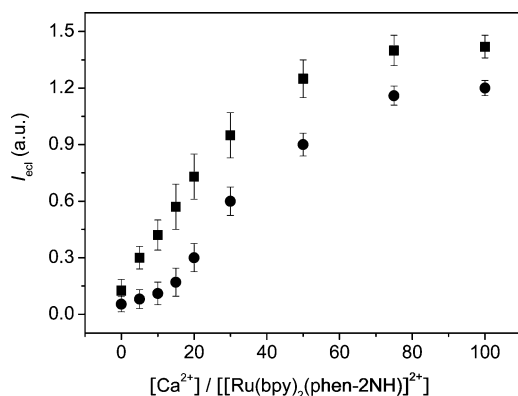


Figure 5. Dependence of the ECL1 (■) and ECL2 (●) intensities on a $[\text{Ca}^{2+}]/[[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}]$ ratio. The ruthenium(II) complex concentration was fixed at 200 μM . Other conditions were the same as those employed in Figure 3.

signals. Similar results were obtained when the potential was swept to the negative direction first, followed by the positive direction. Figure 5 shows the intensities of ECL1 and ECL2 as functions of the concentration ratio of the added Ca^{2+} ions to the complex. A more than 10-fold increase of the ECL signal has been observed when the Ca^{2+} /complex ratio was higher than 50. For other alkaline-earth metal ions, i.e., Mg^{2+} and Ba^{2+} , similar ECL enhancement could be achieved.

The cation-binding effects on ECL generated via coreactant schemes have also been studied. Oxidative-reduction-type ECL of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ involving the coreactant TPrA in an acetonitrile solution was found to be insensitive to the alkaline-earth and transition-metal ions. It has also been found that the presence of TPrA significantly suppressed the enhancement of the photoluminescence of the complex upon the addition of the metal cations. It is believed that the complexation between TPrA and the cations could probably be favorable in competing with the cation binding of the CE moiety of the complex. However, the enhancement of reductive-oxidation-type ECL of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ has been observed upon cation binding. In these experiments, $(^n\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ (2 mM) was used as the coreactant in a

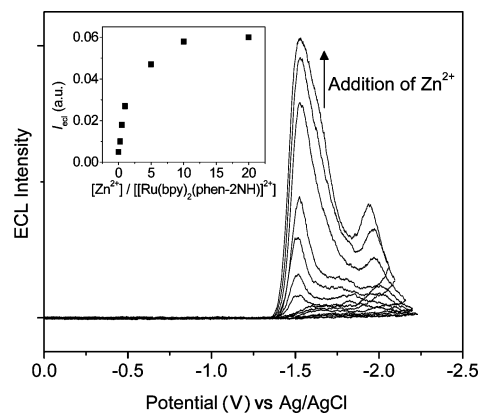


Figure 6. ECL response of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ (2 μM) upon treatment with Zn^{2+} in nonaqueous acetonitrile (0.1 M $^n\text{Bu}_4\text{NClO}_4$). The inset shows the ECL intensity as a function of the $[\text{Zn}^{2+}]/[[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}]$ ratio.

nonaqueous acetonitrile solution and the ECL signal was produced when the potential was swept from 0 to -2.2 V (vs Ag/AgCl). The ECL intensity of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ could be enhanced by ~ 5 -fold in the presence of Mg^{2+} and Ca^{2+} ions and by ~ 10 -fold in the presence of Zn^{2+} ions. The ECL response of the complex upon the addition of Zn^{2+} ions and the ECL intensity as a function of the ratio of Zn^{2+} /complex are shown in Figure 6. These results demonstrated a higher binding affinity of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})]^{2+}$ toward divalent d^{10} transition-metal ions than the alkaline-earth metal ions. The addition of Ba^{2+} or Cd^{2+} ions with a concentration ratio of cation/complex of ~ 2 led to an increase of the ECL intensity by ~ 3 -fold. However, as more concentrated metal ions were added, the ECL intensity started to drop, probably because of precipitation of barium or cadmium sulfate produced in the reactions.

Conclusion

ECL of a series of ruthenium(II) diimine complexes with appended CEs has been studied. The cation-binding effects on the ECL behavior of the ruthenium(II) complexes in acetonitrile solutions with $(^n\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ as the coreactant or via the annihilation scheme were investigated. The results showed that ECL of $[\text{Ru}(\text{bpy})_2(\text{phen-2NH})](\text{ClO}_4)_2$ could be strongly enhanced upon the addition of some alkaline-earth and transition-metal ions.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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