

Solid-State Electrogenerated Chemiluminescence from Gel-Entrapped Ruthenium(II) Tris(bipyridine) and Tripropylamine

Maryanne M. Collinson,* Jacob Taussig, and Skylar A. Martin†

Department of Chemistry, 111 Willard Hall, Kansas State University,
Manhattan, Kansas 66506-3701

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A novel approach for the electrogeneration of stable light emission in a solid host structure under room conditions is described. In this work, the chemiluminescent precursors, ruthenium(II) tris(bipyridine) ($\text{Ru}(\text{bpy})_3^{2+}$) and tripropylamine (TPA), were trapped in a porous silicate host matrix along with an electrode assembly. When the electrode potential was scanned or stepped to a potential sufficient to oxidize gel-entrapped TPA and $\text{Ru}(\text{bpy})_3^{2+}$, electrochemiluminescence (ECL) was observed. The solid-state ECL spectrum was identical to the fluorescence spectrum of gel-entrapped $\text{Ru}(\text{bpy})_3^{2+}$. The intensity of the emission depends on the amount of TPA and $\text{Ru}(\text{bpy})_3^{2+}$ in the gel as well as the size of the electrode. When an ultramicroelectrode (microband or microdisk) was used to generate the ECL, the resultant emission was found to be remarkably stable. Little drop in intensity was observed upon continuous application of ca. 1.2 V for 2–12 h. In direct contrast, the ECL dropped significantly at a large electrode (e.g., $r = 1.1$ mm) in a relatively short period of time. The improved stability of the ECL at ultramicroelectrodes can be attributed not only to their small size, which results in a decreased consumption of TPA, but also to the steady-state flux of reagents to the electrode surface.

Introduction

Electrogenerated chemiluminescence (ECL), the production of light from electrochemically generated reagents, has been an exciting field of research for almost four decades.¹ ECL is particularly well suited for electrochemical and chemical studies due to the simplified optical setup, good temporal and spatial control, and essentially zero background. ECL has proven valuable in the study of highly energetic electron-transfer reactions,^{2–4} in the development of detection methodologies for chemical analysis,^{5,6} and in lasing,⁷ imaging,^{8,9} and scanning optical microscopy¹⁰ applications.

Electrochemically driven *solid-state* light emitting devices have also recently been demonstrated. Solid-state optical materials are an attractive alternative to

solvent based systems due to their greater simplicity, lower cost, and lower toxicity. Electroluminescent (EL) materials prepared by sandwiching conjugated polymers (i.e., the organic semiconductors) between two electrodes and applying a DC voltage across the film have been thoroughly investigated.^{11–13} To a lesser extent, ECL-based materials have also been explored. Wightman, Murray, and co-workers have recently studied the ECL from thin films of poly[RuL_3]²⁺ (where L = vbpy) electropolymerized on platinum-interdigitated array electrodes.¹⁴ Light emission results from the reaction between RuL_3^+ and the RuL_3^{3+} states formed via independent control of the potentials of the closely spaced electrodes.¹⁴ When fixed concentration gradients are established in the film, the system gives rise to ECL emission in the absence of solvent.¹⁴ Elliott and co-workers have also studied the ECL properties of a more

* To whom correspondence should be addressed. E-mail: mmc@ksu.edu. Telephone: 785-532-1468. Fax: 785-532-6666.

† Current address: Department of Chemistry, Truman State University, Kirksville, MO 63501

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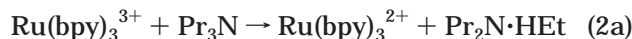
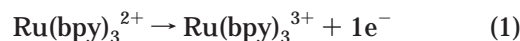
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efficient ruthenium derivative (L = ester-substituted bipyridine) in a sandwich type geometry in the solid state.¹⁵ Under certain conditions, the ECL quantum yields approached those of organic polymer based light-emitting devices.¹⁵ In related work, Rubner and co-workers¹⁶ have also noted solid-state ECL from Ru(bpy)₃²⁺ derivatives trapped in an ionic polymer or fixed to a polymer framework and sandwiched between two electrodes.

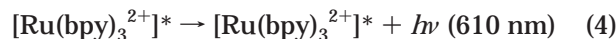
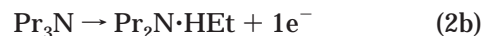
While significant advancements have been made in the development of EL and ECL devices, considerable improvements still need to be made in both the technology and the materials. Higher efficiencies, greater emission intensities, lower operating voltages, and longer device lifetimes are needed.¹¹ ECL-based materials hold considerable promise because the luminescence can be generated with a relatively low voltage bias and with reasonably high efficiency. However, ECL-based materials often suffer from limited stability upon continuous potential excitation due to degradation of the polymer host and/or reaction of the electrogenerated ions with impurities.^{14,17–20}

In this work, an entirely different approach has been utilized to achieve stable ECL in the solid state.²¹ Specifically, the chemiluminescent precursors, ruthenium(II) tris(bipyridine) (Ru(bpy)₃²⁺) and tripropylamine (TPA), have been trapped along with an electrode assembly in a porous, solid host prepared by the sol-gel approach. Sol-gel derived materials provide an attractive alternative to conventional organic polymers due to the ease at which reagents can be introduced into the host framework, their high optical quality, and their good photochemical and electrochemical stability.^{22–24} This particular ECL system was chosen because it allows the luminescence to be generated at a relatively low potential bias in an aqueous environment, thus eliminating the need to work in an inert atmosphere.^{25,26} Emission results when the deprotonated TPA radical formed from upon reduction of Ru(bpy)₃³⁺ or via direct electrode oxidation reacts with another Ru(bpy)₃²⁺ or additional Ru(bpy)₃³⁺ to form [Ru(bpy)₃²⁺]* which then decays to produce orange emission centered at 610 nm. The original Ru(bpy)₃²⁺ species is regenerated during

the reaction albeit TPA is consumed. A simplified ECL reaction scheme for Ru(bpy)₃²⁺-TPA is presented as follows:^{25,26}



or



In a prior communication, we have shown that solid-state ECL can be generated at microdisk electrodes immobilized in a sol-gel derived silica host.²¹ The ECL, although low in intensity, was particularly stable upon continuous potential excitation. In this report, we provide a more detailed account of the ECL generated at ultramicroelectrodes (disks and bands)^{27,28} as well as their long-term stability. These results are very promising in that they demonstrate the applicability of sol-gel hosts and immobilized ultramicroelectrodes to the development of stable solid-state electrochemiluminescence materials for the first time.

Experimental Section

Reagents. Tetramethoxysilane (99%) was purchased from Fluka. Tripropylamine (98%) and ruthenium(II) tris(bipyridine) (98%) were purchased from Aldrich. All reagents were used as received. Deionized water was purified to Type I via a LabConco four-cartridge water purification system.

Procedures. The microdisk electrodes were prepared by heat sealing the Pt microwire (25 μm nominal diameter, Alfa-AESAR) in a tapered glass tube (2.0 mm o.d.) as previously described.²⁷ The microband electrodes were prepared by sealing the metal foil (Alfa) between two glass microscope slides with Epoxy (EPON 828 with 14% (w/w) metaphenylenediamine) and heating sequentially at 75 and 200 °C for 2 h.²⁷ The electrodes were polished with silicon carbide sandpaper and alumina on a napless cloth (Buehler) until smooth. The electrode radius of the Pt ultramicroelectrode was determined to be 13.3 μm from the steady-state limiting current obtained during a slow scan CV (2 mV/s) in 1 mM ferrocene in 0.2 M tetrabutylammonium hexafluorophosphate using a diffusion coefficient of 2.17 × 10⁻⁵ cm²/s.²⁹ The glassy carbon electrode (2 mm diameter) was prepared as previously described.³⁰ The Pt (1.6 mm diameter) electrode was purchased from BAS. A silver chloride coated silver wire reference electrode and the working electrodes were sealed with epoxy in a Nylon cap. Prior to use, the electrodes were polished with 0.05 μm alumina on a napless cloth and thoroughly rinsed with water and ethanol.

The silica sol was prepared via the acid-catalyzed hydrolysis of tetramethoxysilane (TMOS). In a typical preparation, 12 mL of TMOS was mixed with 4.8 mL of water while stirring

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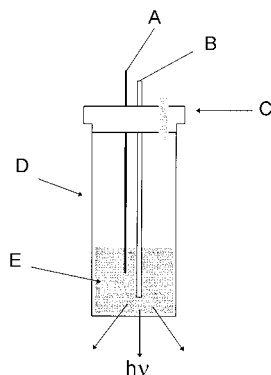


Figure 1. Schematic diagram of the electrochemical cell. It consists of (A) a silver chloride coated silver wire and (B) a Pt ultramicroelectrode (typically $r = 13 \mu\text{m}$) sealed in a small glass tube. Both electrodes are sealed in a nylon cap (C) that is secured in a silanized glass vial (D) containing the doped silica gel (E).

followed by the addition of 1.6 mL of 0.1 M HCl (caution: sol initially becomes very hot with gas evolution). The sol was stirred for 2–3 h, and an aliquot (e.g., 13 mL) was then doped with ruthenium(II) tris(bipyridine) ($\text{Ru}(\text{bpy})_3^{2+}$). The $\text{Ru}(\text{bpy})_3^{2+}$ -doped sol was combined in a 2:1 volume ratio with tripropylamine previously dissolved in either pH 6.2 or pH 7 phosphate buffer (0.1 or 0.05 M) in a previously silanized glass vial that contained the electrode assembly. The total volume of sol in the vial was 3 mL. Gelation occurred almost immediately after mixing. The final mole ratio of TMOS to water was ca. 1:11. The gel was aged for 2–3 days and dried for 1 day at ca. 60–70% relative humidity by exposing a small hole in the Nylon cap (ca. 2 mm dia.). It was necessary to first silanize the glass vials (borosilicate glass, FisherBrand) with chlorotrimethylsilane (6% v/v in hexane, overnight) to prevent the gel from adhering to its surface and thus fracturing upon drying.

The electrochemical cell was placed in a dark box ca. 3.5 cm from the photocathode of a Hamamatsu 4632 photomultiplier tube. This tube was chosen because of its low dark counts (ca. 50–70 counts per second (cps)) at room temperature. A high voltage power supply (Bertan Series 230) applied -800 V to the PMT. The PMT signal was amplified by a fast preamplifier (EGG Ortec VT 120A), and the data were collected with a multichannel scaler (i.e., photon counter, EGG Ortec T-914). For the potential sweep measurements, a BAS 100 potentiostat, previously modified to trigger the multichannel scaler, was used. The potential step experiments were performed with a Pine AFRDE5 bipotentiostat. Fluorescence and ECL spectra were collected on a SPEX Fluoromax-2 fluorimeter with 4 nm spectral resolution. The integration time was set at 16 s for the ECL spectrum and 0.2 s for the fluorescence spectrum.

Results and Discussion

Figure 1 shows a simplified view of the solid-state electrochemiluminescence (ECL) cell. The cell consists of a working electrode (typically a $r = 13 \mu\text{m}$ Pt ultramicroelectrode) and a silver chloride coated silver wire reference electrode imbedded in silica gel monolith housed in a silanized glass vial. The microelectrode was typically placed ca. 2 mm from the bottom of the glass vial. The silica gel monolith was prepared using a two-step procedure: acid-catalyzed hydrolysis of TMOS followed by the base-catalyzed condensation of the silanol groups. Under these conditions, a high pore volume gel will be formed.²² An important requirement in this investigation is that the gel-entrapped chemiluminescent precursors are able to diffuse and react in

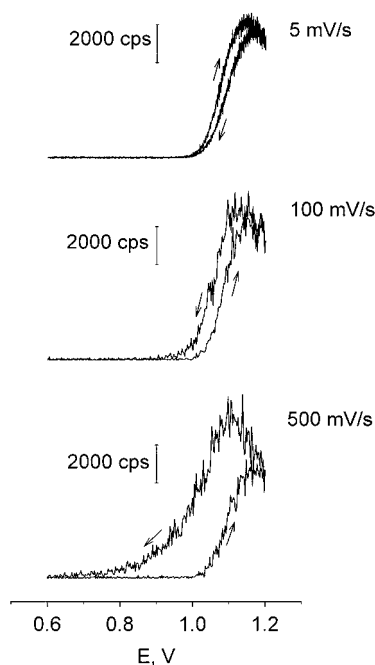


Figure 2. Emission-potential curves for gel-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ (10 mM) and TPA (7 mM) acquired at 5, 100, and 500 mV/s using a $r = 13 \mu\text{m}$ Pt electrode. The gel was prepared with 0.1 M phosphate buffer, pH 7.0. Bin size: 100 ms (5 mV/s), 25 ms (100 mV/s), and 5 ms (500 mV/s, average of four potential scans).

the gel on the local scale. Short drying times were utilized in this work to ensure the gel remains hydrated and is sufficiently porous. Less than 10% reduction in volume was observed after aging and drying the gel for a few days in a high humidity environment. Previous work has shown that the diffusion coefficients of redox molecules trapped with these hydrated solids to be similar to values measured in solution ($10^{-6} \text{ cm}^2/\text{s}$).^{31,32}

The ECL-potential curves for gel-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ at a $r = 13 \mu\text{m}$ Pt ultramicroelectrode acquired at 5, 100, and 500 mV/s are shown in Figure 2. At these scan rates, the cyclic voltammograms (see ref 21) are steady state in nature and superimposed on a relatively large rising background from solvent oxidation.²¹ As shown in prior work, the onset of luminescence is contiguous with the oxidation of gel-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ and/or TPA which occurs near 1.1 V.²¹ In the absence of either TPA or $\text{Ru}(\text{bpy})_3^{2+}$, no significant ECL emission can be observed at the Pt microdisk electrode. At higher sweep rates, the bin size in the photon counter had to be decreased from 100 ms at 5 mV/s to 5 ms at 500 mV/s in order to properly define the shape of the curve. Thus, the data appears “noisier” at the faster scan rates as there are fewer counts per bin.

As can be seen, the shape of the resultant ECL-potential curve is highly dependent on the scan rate. At slow scan rates ($<50 \text{ mV/s}$), the ECL produced during the forward scan occurs at more negative potentials than the reverse scan and has a higher intensity. At higher scan rates ($>100 \text{ mV/s}$), a reversal in position

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and intensity takes place. The ECL is higher on the reverse scan and is shifted to more positive potentials relative to that observed on the forward scan. A drop in the overall ECL intensity was also noted at higher scan rates (> 1 V/s). For the gels prepared with pH 6 phosphate buffer, a noticeable drop in the ECL intensity was observed at scan rates as low as 50 mV/s. At 100 mV/s, the ECL was approximately half that observed at 5 or 10 mV/s.

The overall rate at which this system responds to changes in microelectrode potential will be dictated by the kinetics of the reactions that produce the excited state as well as by the rate of diffusion in the gel. The higher ECL intensity observed at high scan rates during the reverse scan suggests that formation of the deprotonated TPA radical either by direct electrode oxidation of TPA or via chemical oxidation of TPA by $\text{Ru}(\text{bpy})_3^{3+}$ is limiting. In previous work, relative differences in the ECL reaction rate of $\text{Ru}(\text{bpy})_3^{2+}$ with either TPA, oxalate, or proline were evaluated using a stopped flow method.³³ These results showed that the reaction rate is a function of the reducing intermediate, with the $\text{Ru}(\text{bpy})_3^{2+}$ -TPA ECL systems being of intermediate kinetics.

It is not fully understood at the present time why the ECL intensity becomes lower as the electrode potential is scanned significantly past $E_{1/2}$. Given that an ultramicroelectrode was used to generate the emission, the ECL should be steady state at low scan rates.^{27,28} Variations in the ratio of $\text{Ru}(\text{bpy})_3^{2+}$ to TPA from 0.2 to 5 showed similar drops in ECL at large overpotentials and slow scan rates. This drop is not likely due to electrode fouling as repetitive potential scans at 10 mV/s for over 30 min show no diminution in intensity.²¹ Concentration polarization may partially account for the observed decrease. It is also possible that background (solvent) oxidation products (O_2 , H^+) may interfere or otherwise quench the emission and/or $\text{Ru}(\text{bpy})_3^{3+}$ may be consumed during water hydrolysis. The ECL is pH sensitive as a critical step in the reaction mechanism involves deprotonation of radical cation of TPA.^{25,26} Since the measurements are not made in a fully buffered solution, the pH at the electrode surface could be lower during oxidation thus decreasing the ECL intensity. Oxygen is also known to quench the $\text{Ru}(\text{bpy})_3^{2+}$ excited state.

The intensity of the ECL depends on both the concentration of $\text{Ru}(\text{bpy})_3^{2+}$ and the concentration of TPA in the gel. When the concentration of gel-encapsulated TPA was kept constant at either 5 or 10 mM, the ECL intensity increased linearly with $\text{Ru}(\text{bpy})_3^{2+}$ concentration from 1 to 15 mM. Likewise, when the concentration of gel-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ was kept constant at 10 mM, the ECL increased nearly linearly as the concentration of TPA was increased from 2 to 7 mM after which the ECL leveled off.

One of the major concerns in the development of viable solid-state electroluminescent devices for advanced applications is long-term stability. Both solution and solid-state ECL based devices in particular have suffered from poor long-term stability due to the insta-

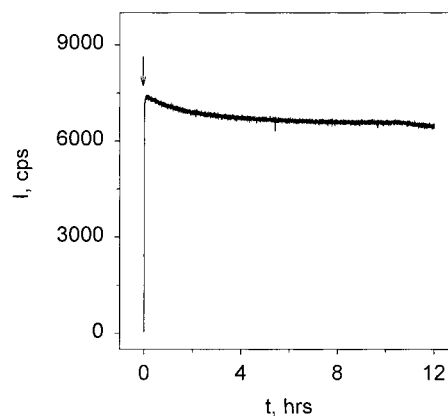


Figure 3. Intensity–time transient for gel-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ (10 mM) and TPA (5 mM) at a $r = 13 \mu\text{m}$ Pt ultramicroelectrode following a potential step to 1.15 V at $t \sim 30$ s for 12 h. The gel was prepared with 0.1 M phosphate buffer, pH 6.2.

bility of the electrogenerated radical ions and/or deterioration of the polymeric host.^{17–20} One of the most promising features of this approach is the remarkable stability associated with the ECL when generated at an ultramicroelectrode. In previous work, no drop in the ECL emission was observed when the electrode potential was repetitively cycled for 30 min at 10 mV/s.²¹ Furthermore, when the electrode potential was stepped to a near diffusion-controlled value, less than a 15–20% loss in ECL was observed for gels prepared with pH 7.0, 0.1 M phosphate buffer and $\text{Ru}(\text{bpy})_3^{2+}$ and TPA concentrations of 2–15 mM.²¹

The long-term stability of the ECL can be improved further by lowering the concentration and/or the pH of the phosphate buffer added to the $\text{Ru}(\text{bpy})_3^{2+}$ -doped sol. Figure 3 shows the ECL obtained in a gel prepared with pH 6.2, 0.1 M phosphate buffer following a potential step to 1.15 V for 12 h. As can be seen, the luminescence increases nearly immediately upon application of the potential step where it remains at a nearly constant level for the duration of the experiment. The ECL is considerably more stable than that reported in other work where a significant drop in intensity has been observed over a 5–30 min time scale.^{14,17–20} Under the current conditions, typically less than a few percent drop in ECL is observed over a 2 h time period. The enhanced stability can be attributed in part to the relative immunity of the $\text{Ru}(\text{bpy})_3^{2+}$ -TPA ECL system to oxygen and water and to the use of ultramicroelectrodes which minimizes reactant depletion at the electrode surface (see below).

The time it takes the ECL to reach maximum intensity after the potential step to 1.15 V is ca. 10–15 s, which is ca. 5–10 times longer than previously described for gels prepared with pH 7 buffer.²¹ This increased rise time is consistent with the observed scan rate dependence of the ECL noted earlier, with the pH ~ 6 gels exhibiting a continuously decreasing intensity as the scan rate is increased. For gels prepared with pH 7 buffer, little difference in ECL intensity with scan rate was noted except at scan rates greater than 1 V/s. This variance in rise times may reflect differences in the kinetics of the ECL reaction (which requires deprotonation of the TPA) in the two different pH gels, and/or it may reflect subtle changes in the structure (porosity)

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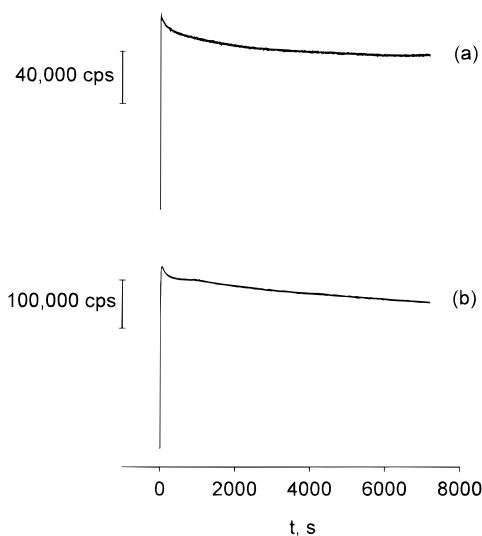


Figure 4. Intensity–time transient for gel-encapsulated Ru(bpy)₃²⁺ (10 mM) and TPA (5 mM) at a (a) 4 μm or a (b) 25 μm Pt band microelectrode ($l \sim 2.8$ mm) following a potential step to 1.2 V at $t \sim 30$ s for 2 h. The gels were prepared with 0.05 M phosphate buffer, pH 7.

of the gel. It will likely be possible to decrease this time by using a system that has faster reaction kinetics such as the Ru(bpy)₃²⁺–oxalate ECL system.³³ Indeed, preliminary results on this ECL system trapped in a gel prepared with pH 6.0 phosphate buffer show that the response time is much quicker (≤ 1 s) than that observed for gel-entrapped Ru(bpy)₃²⁺–TPA.

The ECL intensity can be significantly increased while maintaining long-term stability by using a microband electrode to generate the emission. These electrodes, which are prepared by sealing a piece of metal foil between two glass microscope slides with epoxy, are macroscopic in length (e.g., on the millimeter scale) and microscopic in width (e.g., on the micrometer scale).²⁷ Figure 4 shows the ECL at 4 μm wide Pt (Figure 4a) and 25 μm wide Pt (Figure 4b) microband electrodes ca. 2.8 mm length. As with the microdisk electrodes, the ECL reaches a maximum value within 10–15 s after the electrode potential is stepped from 0.6 to 1.2 V where it remains nearly constant for the duration of the experiment. As can be noted, the ECL is significantly larger and is nearly as stable as that observed at microdisk electrodes. For the 4 μm Pt band electrode, the increase in ECL relative to that observed for the microdisk electrode approximately correlates with the increased electrode area, taking into consideration slight differences in collection efficiency of the PMT and placement of the electrode in the gel.

The enhanced stability of the ECL observed at the ultramicroelectrodes can be attributed not only to their small size, which results in a decreased consumption of TPA, but also to the steady state flux of reagents to the electrode surface. For an ultramicroelectrode, the dimensions of the diffusion layer greatly exceed that of the electrode in a relatively short period of time (e.g., seconds). Because a greater population of TPA molecules are then able to diffuse to the electrode from the greater solid angle around the electrode, steady state is reached quickly.^{27,28} This steady state or quasi-steady-state flux of material to the electrode surface is also apparent in the ECL time profiles obtained at a microband elec-

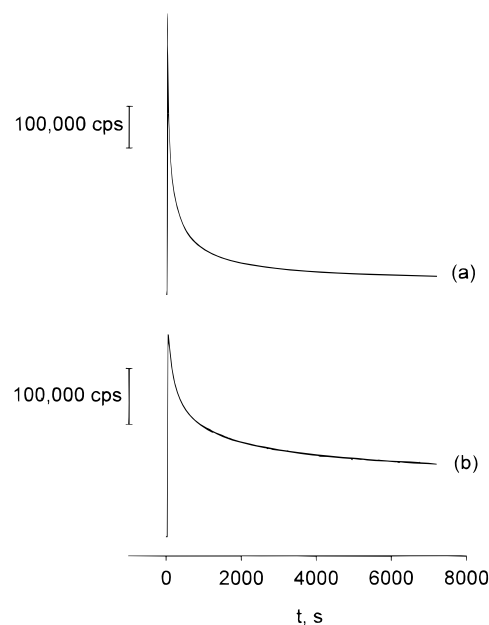


Figure 5. Intensity–time transient for gel-encapsulated Ru(bpy)₃²⁺ (10 mM) and TPA (5 mM) at a (a) $r = 1.1$ mm glassy carbon disk or a (b) 0.8 mm Pt disk following a potential step to 1.2 V at $t \sim 30$ s for 2 h. The gels were prepared with 0.1 M phosphate buffer, pH 6.2. An 1.0 optical density filter was used in this experiment to avoid saturation of single photon counter.

trodes. While these electrodes are macroscopic in length, they are microscopic in width.^{27,28} The magnitude of the luminescence is determined by the largest dimension of the electrode whereas its “steady-state behavior” is determined by its width. Thus, the ECL intensity is considerably higher when generated with a microband electrode whereas the luminescence is nearly as stable because of the quasi-steady-state flux of reagents to the microscopic electrode surface.^{27,28}

In distinct contrast, when a macroscopic disk electrode is used to generate the chemiluminescent precursors, the ECL intensity drops dramatically due to the greater consumption of reagents and their subsequent depletion at the electrode surface. Figure 5 shows the ECL obtained at a $r = 1.1$ mm glassy carbon (Figure 5a) and $r = 0.8$ mm platinum disk (Figure 5b) electrode after the electrode potential is stepped to 1.2 V for 2 h. A neutral density filter was utilized in these experiments to avoid saturating the photon-counting equipment during the initial potential step. As can be seen, the ECL decays rapidly during the first 30 min and then drops slower for the duration of the experiment. A similar drop in ECL was also observed when the electrode potential was repetitively cycled. At a large disk electrode, the diffusion layer thickness is considerably smaller than the electrode radius during a significant portion of the potential step. As a result, the ECL drops as TPA is consumed and the resultant depletion layer extends into the bulk gel. Convective transport of reagents will likely be minimal due to the rigidity of the gel. At relatively long times, the ECL becomes pseudo steady state in appearance. As expected, the rate at which the ECL drops and the time it takes to reach a nearly constant level depends on the size of the electrode. Larger electrodes show a larger drop in the ECL and take longer to reach a steady state like level than smaller diameter electrodes. The rather rapid

initial drop in ECL observed at the glassy carbon electrode may also be partially due to surface adsorption in addition to reagent depletion as carbon electrodes are prone to adsorption.

The ECL is of sufficient intensity and stability at the microband electrode to obtain a solid-state ECL spectrum for this system. Figure 6 shows a direct comparison of the ECL spectrum obtained at a 4 μm Pt band microelectrode with the fluorescence spectrum obtained using an excitation wavelength of 450 nm. Both spectra were collected in a SPEX fluorimeter with a spectral bandwidth of 4 nm. The fluorescence maximum is located at 412 nm which is consistent with that obtained for $\text{Ru}(\text{bpy})_3^{2+}$ in solution as well as in a hydrated silica host structure.^{34,35} As can be seen, the ECL spectrum is nearly identical to the fluorescence spectrum, which is expected since the emitting state in both cases is the ³MLCT of $\text{Ru}(\text{bpy})_3^{2+}$. This is also consistent with solution-based studies which previously showed the equivalency between the ECL and fluorescence spectra of $\text{Ru}(\text{bpy})_3^{2+}$.³⁶

Conclusions

Sol-gel derived solids provide a viable environment in which to entrap chemiluminescent precursors. The microscopic fluidity of the matrix allows the chemiluminescent reagents to be electrochemically generated in situ whereas the microscopic rigidity of the host significantly reduces convection and eliminates the need for excess solvent and flowing streams. In this work, solid-state electrogenerated chemiluminescence was observed for gel-entrapped $\text{Ru}(\text{bpy})_3^{2+}$ and TPA. The ECL was found to be stable for periods in excess of 24 h when generated with an ultramicroelectrode (micro-disk or microband) assembly. Theoretically, based on the amount of TPA in the gel and the geometric size of the microelectrode, the ECL should be stable for several months to years. The stability of this system can be attributed primarily to the relative immunity of the $\text{Ru}(\text{bpy})_3^{2+}$ -TPA system to water and oxygen as well as to the use of an ultramicroelectrode assembly. The small size of the electrode results in a decreased consumption

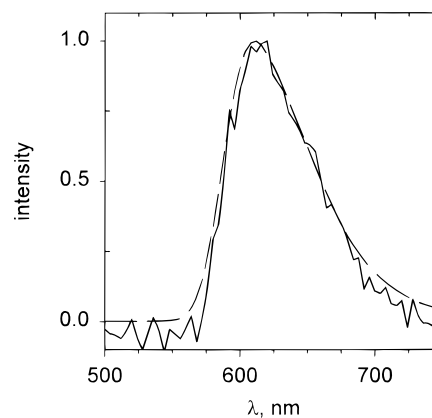


Figure 6. Direct comparison of the fluorescence spectrum (dashed line) with the ECL spectrum (solid line) obtained for gel-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ (10 mM) and TPA (5 mM). The gel was prepared with 0.1 M phosphate buffer, pH 6.2. The ECL spectrum was obtained at a 25 μm Pt band microelectrode ($l \sim 2.8$ mm) following a potential step from 0.6 to 1.2 V. The fluorescence spectrum was obtained using an excitation wavelength of 450 nm.

of TPA while at the same time it provides a constant or nearly constant flux of reagents to the electrode surface. At a large macroscopic electrode, the ECL drops quickly due to the depletion of reagents at the electrode surface. It may be feasible to increase the ECL intensity while maintaining stability via optimization of electrode geometry and size, the porosity and polarity of the host, and/or utilization of other more efficient electroluminescent systems. Different emission wavelengths can also likely be achieved through variations in the precursor molecules. Future investigations will be directed in this manner.

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