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Electrogenerated Chemiluminescence in Polyelectrolyte Multilayers: Efficiency and Mechanism

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The presence of an ultrathin film of polyelectrolyte complex, formed by the multilayering method, on an electrode was shown to enhance the intensity of electrogenerated chemiluminescence (ECL) from the tris(2,2')bipyridylruthenium(II)/tripropylamine system. Platinum electrodes coated with up to 17 layers of poly(diallyldimethylammonium chloride) or poly(vinylmethylpyridine), alternately layered with poly(styrenesulfonate), revealed significant differences in enhancement of ECL, depending on the identity of the multilayer. ECL following deposition of each layer showed an oscillating intensity of light emission, which alludes to the importance of surface and bulk charge. This effect, along with others, such as increased output with increasing tripropylamine concentration, was used to suggest a mechanism for enhanced ECL intensity at multilayer-coated electrodes.

Electrogenerated chemiluminescence¹ (ECL) is an electrochemically induced process in which light is emitted from an excited species. Excitation is achieved by direct oxidation of luminescent species or, indirectly, by using an intermediate or coreactant.^{2–5} ECL has been used in the clinical diagnosis of thyroid disease^{6,7} and tumors^{8–12} and has also been applied in cardiac markers,¹³ environmental assays,¹⁴ integration with HPLC and CE^{15,16} columns, and chemical warfare agent detection.³ In

other examples, capillary electrophoresis microchips have integrated ECL detection methods.^{17–19} The majority of commercially available ECL schemes are implemented with tris(2,2')bipyridylruthenium ($\text{Ru}(\text{bpy})_3^{2+}$) along with tripropylamine (TPrA) derivatives as coreactant. For example, one assay uses paramagnetic beads as a support phase.²⁰ $\text{Ru}(\text{bpy})_3^{2+}$ -TPrA-labeled products are bound to these beads and passed into a flow cell. A magnet captures the beads on the surface of an electrode in the flow cell, effectively separating the labeled products from unbound labels and other compounds in the assay matrix. Applying an electrical potential to the electrode excites $\text{Ru}(\text{bpy})_3^{2+}$ -TPrA labels near the surface of the electrode.²⁰ Tumor markers are often detected and analyzed clinically using $\text{Ru}(\text{bpy})_3^{2+}$ ECL methods.²¹ Cancer screening and fertility-related tests are also possible.^{22–27} Low limits of detection are achieved with optical array detectors in DNA assays.²⁸ For example, a lower detection limit of HIV DNA of fewer than five copies has been cited for ECL coupled to polymerase chain reaction amplification.²⁹

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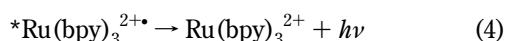
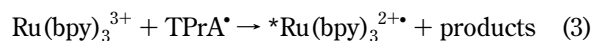
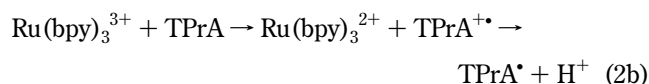
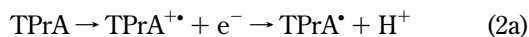
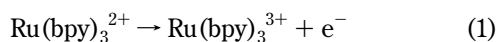
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The Ru(bpy)₃²⁺–TPrA system has been the focus of research aimed at understanding the mechanism for light emission and enhancing its efficiency.^{30,31} One accepted scheme³² is presented in

Scheme 1.

Proposed Ru(bpy)₃²⁺–TPrA ECL Reaction Sequence³²



The sequence starts with oxidation of Ru(bpy)₃²⁺ (1) and continues with direct (2a) or indirect (2b) oxidation of TPrA (2a). A tripropylamine radical reduces Ru(bpy)₃³⁺ to an excited state *Ru(bpy)₃²⁺ (3), which is thought to emit on relaxation (4). The typical emission is broadly centered at ~620 nm with cited instances at 700 nm in surfactant solution.³³ TPrA oxidation is thought to be important at the low ruthenium(II) concentration usually employed in ECL experiments.³⁴ Ru(bpy)₃²⁺ is often transported to the electrode from solution. Alternatively, it may be localized at the electrode surface by various methods such as adsorption on negative nanoparticles³⁵ or immobilization within films on the electrode surface.³⁶

The efficiency of light production, in terms of photons emitted versus electrons transferred, is relatively low and the use of costly Ru(bpy)₃²⁺ is a concern. The surface morphology and structure of the electrode has been shown to impact ECL efficiency.³⁷ It has been noted that oxide layers on Pt and Au electrodes influence light production.³⁸ Recently, it was shown that a hydrophobic surface film on the electrode enhanced luminescence efficiency severalfold.^{34,39} Here, we investigate the use of polyelectrolyte multilayer^{40,41} (PEMU) film coatings^{42,43} for transporting ECL-active molecules. PEMUs are robust thin films highly suited to im-

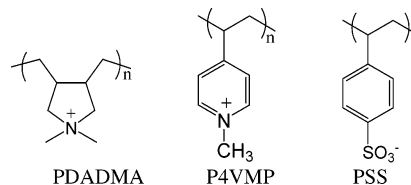


Figure 1. Polyelectrolytes used in the layer-by-layer deposition sequences. From left to right, poly(diallyldimethylammonium), poly(4-vinylmethylpyridinium), and poly(styrenesulfonate).

mobilizing biomolecules,⁴⁴ such as enzymes⁴⁵ and antibodies,⁴⁶ for various assays.⁴⁷

Previous work⁴³ investigated direct ECL from a multilayer of DNA and poly(vinylpyridine) (PVP) bearing [Ru(bpy)₂]²⁺ units. A square wave voltammetric waveform oxidized the Ru²⁺, and ECL during the catalytic oxidation was measured simultaneously. ECL was also found to result from PEMUs made with [Os(bpy)₂-(PVP)₁₀]²⁺, which is easier to oxidize, and chemically oxidized DNA.⁴² When combined with [Ru(bpy)₂(PVP)₁₀]²⁺, this latter system could be used to detect DNA oxidation and nucleobase adducts from chemical damage.³³ Our current work investigates ECL generated from the Ru(bpy)₃²⁺–TPrA system diffusing through an ultrathin PEMU assembled from cationic polymers poly(diallyldimethylammonium chloride) (PDADMAC) or poly(4-vinylmethylpyridinium) (P4VMP) and an anionic polymer, poly(styrenesulfonate) (PSS). Significant enhancements in ECL efficiency as well as insight into the mechanism were obtained.

EXPERIMENTAL SECTION

Materials. PDADMAC (Aldrich), $M_w = 3.69 \times 10^5$, $M_w/M_n = 2.09$; PSS (Scientific Polymer Products), $M_w = 57\,500$, $M_w/M_n = 1.03$, were used as received. Poly(4-vinylmethylpyridinium iodide), $M_w = 65\,500$, was purchased from Polysciences Inc. NaCl was from Fluka. All solutions were made with 18-M Ω deionized H₂O. Structures of polyelectrolytes used are shown in Figure 1.

ECL solutions comprised 10^{−5} M tris(2,2′)bipyridylruthenium-(II) and 0.05 M TPrA (both from Aldrich) solution maintained at pH 7.2 by 0.2 M phosphate buffer. In some experiments, NaCl was added.

Instrumentation. Potential was controlled with an EG&G Princeton Applied Research model 362 potentiostat. ECL was amplified by a 13-mm-diameter, nine-stage, side-on type Hamamatsu photomultiplier tube (PMT), model R3823, powered by a Bertan Associates 313B power supply set at 901 V. The PMT was positioned at a distance of 1 cm from the working electrode.

The electrochemical cell was enclosed in a dark box, built in-house, with dark current of <1 nA. The solution volume was 25 mL. The platinum grid counter electrode, 4.5-cm² area and ~60% transparent, was coplanar with the working electrode and between the working electrode and the PMT. The working electrode was a platinum foil, 2 cm long and 0.5 cm wide, and the reference was a KCl-saturated calomel electrode (SCE). The Pt was cleaned

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in 70% H_2SO_4 (concentrated)/30% $\text{H}_2\text{O}_{2(\text{aq})}$ ("piranha": *caution*, piranha is a strong oxidizer and should not be stored in closed containers) and rinsed in distilled water. The solution was continuously and vigorously stirred with a propeller stir rod on the end of a small motor.

ECL currents from the PMT were recorded with a Keithley 617 electrometer, and electrochemical cell currents were read from the potentiostat with a Keithley 196 multimeter. Data from the meters were collected via their IEEE ports on a PC running Labview 6 (National Instruments). ECL measurements during cyclic voltammetry scans, between 0.7 and 1.5 V,⁴⁸ on bare and coated platinum electrodes showed a peak in light intensity at 1.19 V, during both the oxidizing and reducing runs.

Multilayer thickness was determined using a Gaertner Auto-gain L116 S ellipsometer with 632.8-nm radiation at 70° incident angle. A refractive index of 1.55 was used for all PEMUs.

Multilayer Buildup with ECL. Construction of multilayers started with the positive polyelectrolyte (PDADMAC or P4VMP) due to the negative charge on the bare Pt (or oxide) surface. Sequential deposition on the working electrode was done with a 5-min dip in the polyelectrolytes (1 mM concentration based on the repeat unit, in 0.4 M NaCl) with an intermediate rinse in 0.4 M NaCl. ECL measurements were taken immediately after each polyelectrolyte deposition step. The ECL solution contained no salts other than the 0.2 M phosphate buffer, which served as supporting electrolyte. The average dry thickness of 16 layers on surrogate silicon wafers (which permitted ellipsometric measurements) was 669 Å for PDADMA/PSS and 285 Å for P4VMP/PSS. PEMUs are extremely reproducible with respect to thickness^{49,50} and can be built on a plethora of substrates, including platinum.⁵¹ Once built, the PEMUs are very durable and do not disassemble unless subjected to solutions of high ionic strength (the upper stability limit for PDADMA/PSS is ~2.5 M NaCl).

ECL with Varying NaCl Concentration. The ECL behavior of a fixed number of layers with changing salt concentration was investigated using 16 and 17 layers of PDADMA/PSS or P4VMP/PSS built on the Pt electrode. These PEMUs were allowed to anneal in 1 M NaCl solution for 24 h. Cell current and ECL current were recorded at constant applied potential (1.19 V vs SCE) for salt concentrations in the 0.1–0.6 M NaCl range. Aliquots, 200 μL each of 5.32 M NaCl, were injected sequentially into the electrolyte with stirring. The potentiostat was left in the "on" position to avoid the brief surge in current that occurred every time the circuit was turned on. The luminescent system was allowed to stabilize for 1 min, after which time the light intensity reached steady-state conditions. Reproducibility of steady-state luminescence was $\sim\pm 5\%$ RSD from run to run. Reproducibility between different identically treated electrodes was $\sim\pm 10\%$ RSD, as the electrodes had to be manually placed in the same position with respect to the PMT. An apparatus with fixed electrode and PMT positions would improve the variability.

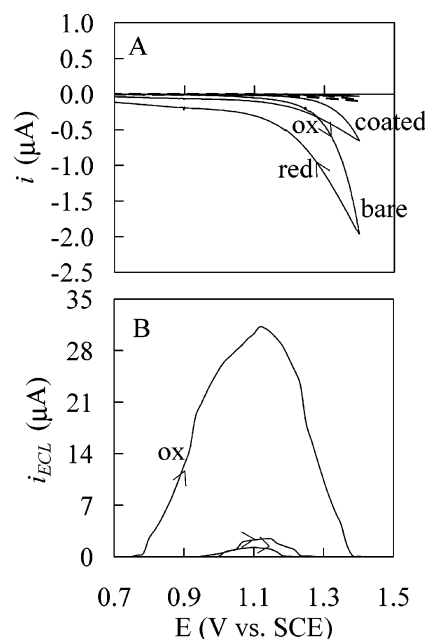


Figure 2. (A) CV for the $\text{Ru}(\text{bpy})_3^{2+}$ (10^{-5} M)–TPrA (0.05 M) ECL solution on bare and PDADMA/PSS-coated electrodes. The dotted lines showing background CV currents without $\text{Ru}(\text{bpy})_3^{2+}$ or TPrA. (B) ECL vs potential for anodic sweep, upper curve for 16 layers of PDADMA/PSS; middle curve for P4VMP/PSS, 16 layers, and lower curve for the bare electrode. In both multilayers, the outermost layer was PSS (negative). Conditions: 50 mV s^{-1} scan rate, 1- cm^2 electrode area, in 0.2 M NaH_2PO_4 , pH 7.2 with no extra NaCl added.

RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)–ECL. CV, with simultaneous measurement of ECL, was used to determine which potential induced the highest luminescence output on 16 layers of PDADMA/PSS and P4VMP/PSS. As shown in Figure 2, which presents electrochemical cell current passing through the multilayer, i_{PEMU} , and the photomultiplier current, i_{ECL} , repeated CVs established that the system is brightest at ~1.19 V (consistent with previous literature⁵²) on both the oxidation and reduction directions. This potential on the cell current plot corresponds to a chemically irreversible and otherwise uneventful region. The fact that the ECL peak output comes well before the maximum in electrochemical current (~1.35 V) is due to the complex chemically coupled processes, summarized by example in eqs 1–4, that are required to produce light. Several chemical reaction steps follow the electrochemical oxidation of the $\text{Ru}(\text{bpy})_3^{2+}$ species. Immediately apparent is the significant enhancement (~25-fold), in light output with one of the PEMU-coated electrodes compared with bare Pt (Figure 2). All other variables in the system remain the same, and the additional light is produced with even less cell current than in the bare electrode case.

The present luminescent system has two components that coreact in order to yield light. TPrA has a K_b of 10.4, and at an experimental pH of 7.2 (phosphate buffer),⁵² it exists mostly in its protonated form. After oxidation, the following proton transfer is thought to occur near the electrode.⁵³ For PEMU-modified

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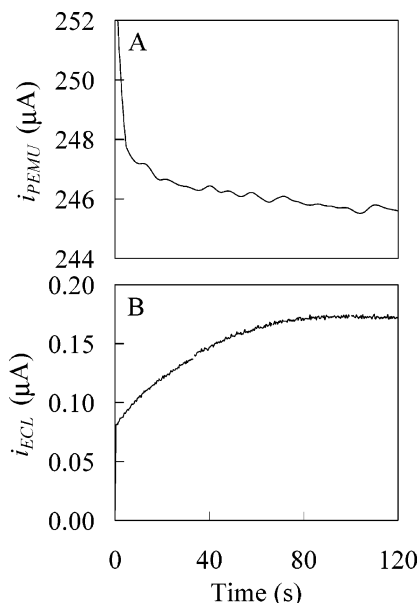


Figure 3. Membrane current and ECL behavior vs time of a 16-layer PDADMA/PSS PEMU in 0.5 M NaCl. $E = 1.19$ V vs SCE, on a 1-cm² platinum electrode. ECL solution consisted of 10⁻⁵ M Ru(bpy)₃²⁺ and 0.05 M TPrA at pH 7.2 in 0.2 M phosphate buffer.

electrodes, the proton transfer occurs inside the thin film: $\text{TPrAH}^+ + \text{HPO}_4^{2-} \rightarrow \text{TPrA} + \text{H}_2\text{PO}_3^-$.

Chronoamperometry: Steady-State Currents. When the electrode was poised at oxidizing potentials, and the redox current monitored versus time, the expected initial decay was observed, with approximate leveling off after ~10 s as the current reached a pseudo steady state due to convection-diffusion mass transport.

The luminescent output versus time showed surprising behavior: i_{ECL} increased at first before reaching steady state after ~60 s. Both the increase versus time and part of the overall enhancement of luminescence can be explained by a mechanism of transient buildup of electrogenerated Ru(bpy)₃³⁺ at the electrode within multilayer.

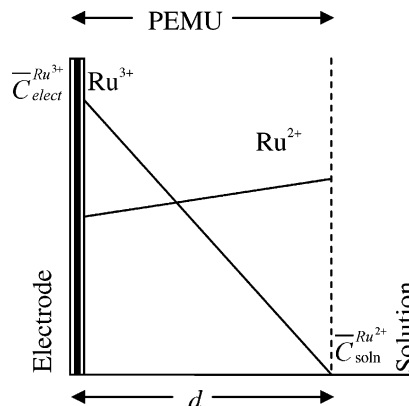
It is known that ions of lower charge tend to diffuse more rapidly through a PEMU.^{54,55} In an extensive study of this phenomenon, we posited an ion hopping mechanism, where salt ions doped into the PEMU structure under the influence of salt concentration in the solution provide sites for ion exchange and ion hopping.⁵⁶ Ions with higher charge require coincidence of more sites within a multilayer to move. The hopping statistics were reproduced by Monte Carlo simulations and also by explicit probability expressions. The diffusion coefficient was found to scale with salt concentration as follows:⁵⁵

$$D \sim y^n \quad (5)$$

where y is the NaCl concentration present in the multilayer and n represents the charge of the probe species.

This interesting dependence of mobility on ion charge was exploited in a device with a PEMU membrane that acted as a rectifier, allowing the preferential passage of ions with lower

Scheme 2. Illustrative Concentration Profiles through the PEMU Membrane for the Oxidation of a Solution Containing Ru(bpy)₃²⁺ to Ru(bpy)₃³⁺^a



^a The electron transfer takes place at the electrode surface. The membrane concentration of Ru(bpy)₃³⁺ is lower than that of Ru(bpy)₃³⁺ since the former diffuses much faster. The concentration profile of Ru(bpy)₃²⁺ is almost uniform as the oxidation rate is limited mainly by electron-transfer kinetics.

charge, and suggesting transistor-like applications.⁵⁷ In the present case, Ru(bpy)₃²⁺ is converted to Ru(bpy)₃³⁺ at the electrode surface. Since the electrochemical current at 1.19 V has not yet reached the diffusion-limited case (where the surface concentration of Ru(bpy)₃²⁺ $\rightarrow 0$), the oxidation rate of Ru(bpy)₃²⁺ is mainly limited by charge-transfer kinetics. The Ru(bpy)₃³⁺ that is produced, however, is limited much more by diffusion and therefore accumulates within the PEMU, where it reacts with TPrA as shown in Scheme 1.

At steady state, the following flux balance equations may be written:

$$J_{\text{Ru}^{2+}} = -J_{\text{Ru}^{3+}} = \frac{\bar{D}_{\text{Ru}^{3+}} \bar{C}_{\text{elect}}^{\text{Ru}^{3+}}}{d} \quad (6)$$

where J is the flux, d is the multilayer thickness, $\bar{C}_{\text{elect}}^{\text{Ru}^{3+}}$ refers to the concentration at the electrode, and $\bar{D}_{\text{Ru}^{3+}}$ is the diffusion constant of Ru(bpy)₃³⁺ through the film.

The concentration profiles in Scheme 2 depict a buildup of Ru(bpy)₃³⁺ compared to Ru(bpy)₃²⁺ within the PEMU due to slower Ru(bpy)₃³⁺ transport. For a stirred system, the Ru(bpy)₃³⁺ concentration at the PEMU/solution interface $\rightarrow 0$. The profile of Ru(bpy)₃²⁺ reflects the fact that the Ru(bpy)₃²⁺ is not being reduced at its diffusion-limited rate, and thus, the concentration at the electrode surface does not $\rightarrow 0$.

Layer-by-Layer Buildup with ECL. Both redox and luminescent currents exhibit oscillatory behavior when the PEMU is built layer by layer (Figure 4). At fixed potential, the redox current, which depends on the oxidation of Ru(bpy)₃²⁺, decreases substantially on the first layer but does not decrease thereafter, in contrast with prior work on this kind of layer-by-layer buildup.^{55,58} The difference is due to the fact that, in the present case, the oxidation current is limited mainly by electron-transfer kinetics,

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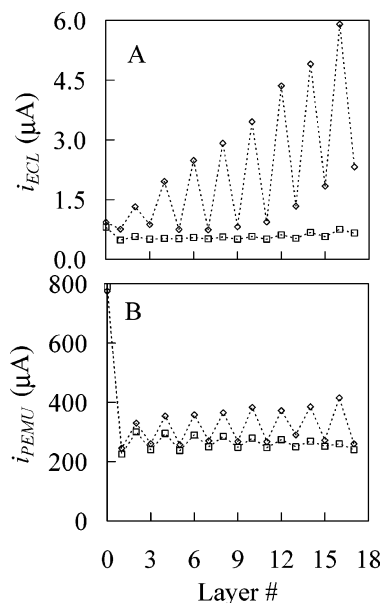


Figure 4. Steady-state electrochemical and ECL intensity during a layer-by-layer buildup; diamonds, PDADMA/PSS data; squares, P4VMP/PSS data. Panel A shows the ECL currents, and panel B shows membrane current through the PEMU. $E = 1.19$ V vs SCE, on a 1-cm² platinum electrode, 10^{-5} M Ru(bpy)₃²⁺ and 0.05 M TPrA at pH 7.2, in 0.2 M phosphate buffer. Each polyelectrolyte was deposited from 0.4 M NaCl. The thicknesses of PDADMA/PSS and P4VMP/PSS PEMUs at 16 layers were 669 and 285 Å, respectively.

and the film is not a significant barrier to Ru(bpy)₃²⁺ transport at this potential.

Redox currents increase slightly following the addition of the negative (PSS) layer. This is probably due to enrichment of the positive Ru(bpy)₃²⁺ species within the membrane by the negative surface charge, in a classical ion exchange fashion. Luminescence currents also oscillate as layers are added in sequence, as shown in Figure 4B. The most intense light output is again provided with PSS as the outermost layer. The fact that the oscillation is more accentuated with luminescence than with redox currents is of interest. A greater flux of Ru(bpy)₃²⁺ would generate more Ru(bpy)₃³⁺, but the increase in light output is greater than would be anticipated by inspection of the redox current in Figure 4A. It is likely that the negative surface also increases the membrane concentration of TPrA, which is positively charged under the conditions of our experiments. As shown below, TPrA concentration is a key variable in light output.

A comparison of the properties of the PDADMA/PSS and P4VMP/PSS multilayers further reinforces the importance of surface charge. P4VMP builds thinner films than PDADMA, yet the redox current through both is the same, consistent with a redox current limited by charge-transfer kinetics. The oscillations in light output are less extreme for the P4VMP because the layer of surface charge is thinner and collects less Ru(bpy)₃²⁺ and TPrA. Furthermore, we have found, using in situ FT-IR studies,⁵⁹ that the concentration of ions within the bulk of P4VMP/PSS multilayers is about half of that within PDADMA/PSS films—direct

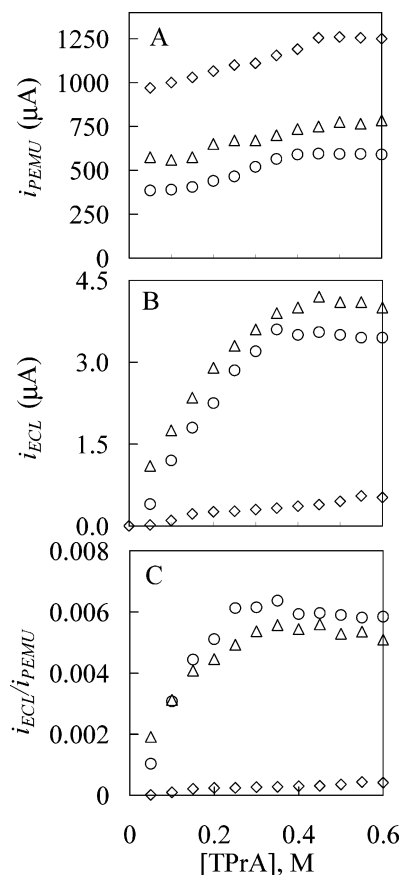


Figure 5. Steady-state membrane current, ECL current, and efficiency vs TPrA concentration for a 16-layer PSS–PDADMA PEMU. Panel A shows the cell currents for 16 layers (triangles) with PSS on top and 17 layers (circles) with PDADMA on top. Data for the bare electrode are depicted by diamonds. Panel B shows the ECL currents, and panel C compares relative efficiencies. Data were recorded at $E = 1.199$ V vs SCE, on a 1-cm² platinum electrode, 10^{-5} M Ru(bpy)₃²⁺ and 0.05 M TPrA at pH 7.2, in 0.2 M phosphate buffer.

evidence of enhanced sorption of charged species in PDADMA/PSS. Greater luminescence enhancement with the PDADMA multilayer, compared to the P4VMP system, is attributed to greater permeability and greater membrane ion concentration of the former.

ECL at a Fixed Potential with Varying NaCl Concentration.

In prior studies on ion transport through PEMUs, the concentration of salt (usually NaCl) in solution was shown to play a major role.^{57,60–63} In general, additional salt enhanced ion flux considerably. In the present case, salt concentration was found to play a minor part in redox current. For example, redox and ECL currents decreased gradually as salt concentration increased. (See Supporting Information.) Salt probably leads to exchange of Ru(bpy)₃²⁺ by Na⁺ ions, especially at the surface of the PEMU. If the oxidation of Ru(bpy)₃²⁺ were proceeding at the convection–diffusion limited rate, reduction of membrane current would be expected due to increased solution viscosity. In contrast, the

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reduction in current occurs mainly at lower salt concentration. The relative efficiency, the ratio of ECL current to membrane current, does not appear to be impacted much by the presence of NaCl, even at high concentration.

ECL at a Fixed Potential with Varying TPrA Concentration. TPrA is a coreactant in the pathway for light generation, as shown in Scheme 1. Prior work on ECL using the $\text{Ru}(\text{bpy})_3^{2+}$ -TPrA system demonstrated that light emission depends on TPrA concentration.⁵³ As shown in Figure 5, ECL increases as TPrA concentration increases up to ~ 0.4 M. The redox current also increased slightly, possibly because of direct oxidation of TPrA (Scheme 1, eq 2a). Also shown in Figure 5 is the ratio of ECL to redox current, a measure of the relative efficiency of the ECL process. This suggests that in our case, reaction steps 2a and 2b are rate limiting up to 0.4 M TPrA and at higher TPrA oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ (step 1) is the rate-limiting step. Note that ECL continues to increase at the bare electrode since $\text{Ru}(\text{bpy})_3^{2+}$ oxidation is somewhat faster.

Our data also show an increase in i_{ECL} with increasing TPrA concentration. The relationship is not linear however, as i_{ECL} levels off. ECL for the P4VMP/PSS system (see Supporting Information) behaves similarly although at the highest TPrA concentration i_{ECL} actually decreases. At sufficiently high concentration, the TPrA cation may actually displace $\text{Ru}(\text{bpy})_3^{2+}$ from the film.

CONCLUSIONS

In summary, coating by the appropriate polyelectrolyte multilayer can increase the luminescence efficiency of an ECL system substantially. It is believed that the preferential transport of species of lower charge within multilayers is responsible for enhancing

the ECL output, even though the redox current decreases. The choice of PEMU system for achieving greater ECL efficiency is not trivial, as demonstrated by a comparison between multilayers made with different polycations. Extrapolating from prior work on hydrophobic coatings³⁹ might lead one to believe that the more hydrophobic PEMU will generate more ECL. This is not the case, as the PDADMA multilayer contains more water. Since the construction of multilayers on various substrates is straightforward, it is envisaged that existing analytical platforms based on ECL can be modified rapidly to enhance the number of photons per electrochemical event. PEMU coating may be deposited on microchips, microfluidic channels, and arrays of electroluminescent probes.

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SUPPORTING INFORMATION AVAILABLE

Plots showing the membrane current and ECL current through PDADMA/PSS and P4VMP/PSS PEMUs with varying NaCl and TPrA concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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