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Solid-State Light-Emitting Devices Based on the Tris-Chelated Ruthenium(II) Complex: 3. High Efficiency Devices via a Layer-by-Layer Molecular-Level Blending Approach

A. Wu, D. Yoo, J.-K. Lee,[#] and M. F. Rubner*

Contribution from the Departments of Materials Science and Engineering and Chemistry, Massachusetts Institute of Technology, Cambridge Massachusetts 02139

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Abstract: High efficiency, solid-state light-emitting devices have been fabricated from a water soluble, polymeric ruthenium (II) complex, $Ru(bpy)_3{}^{2+}$ polyester, via the use of a layer-by-layer processing scheme. Spin-coated devices of this material were found to produce maximum luminance levels of $250-300$ cd/m^2 with an external quantum efficiency of 0.2% photons/electron. Devices based on sequentially adsorbed layers of the $Ru(bpy)_3{}^{2+}$ polyester and poly(acrylic acid), on the other hand, exhibit external quantum efficiencies in the $1-3\%$ range with a maximum light output of $40-50$ cd/m^2. These high device efficiencies were obtained by optimizing the relative amounts of $Ru(bpy)_3{}^{2+}$ polyester and poly(acrylic acid) incorporated into the film via a layer-by-layer molecular-level blending approach. Through this type of control, it was also possible to create compositionally graded heterostructures and to produce devices that emit light only in the forward or reverse bias or that were completely symmetrical (similar light output, current flow, and efficiency in both forward and reverse bias).

Introduction

In this series of papers, we have been exploring the use of the tris-chelated polypyridyl ruthenium (II) complex as an active light emitter in thin film solid-state devices. Polypyridyl Ru(II) complexes are well-known for their ability to produce light in a process known as electrogenerated chemiluminescence (ECL).[1−10] Only recently, however, has it been demonstrated that it is also possible to utilize these materials in thin film solid-state devices.[11−16] Detailed studies concerning the mechanism of the solid-state behavior of the Ru(II) complex in light-emitting devices have also recently been reported.[17,18] All results to date indicate that the mechanisms of charge injection and transport active in solid-state devices based on the Ru(II) complex are associated primarily with the electrochemistry of this complex.

Some of the critical parameters that need to be controlled when attempting to fabricate high efficiency, high light output electrochemically driven solid-state devices include (1) the level of ionic conductivity, (2) film thickness, (3) the average site-to-site distance and molecular environment of the Ru(II) complexes, and (4) electrode and self-quenching effects. Some level of ionic conductivity is needed to facilitate the spatial redistribution of counterions that must occur when the mixed valent Ru(III/II) and Ru(II/I) states are created at the anode and cathode, respectively. The use of thin films (<2000 Å) helps to overcome the limited ionic and electronic conductivities typical of these systems. The average site-to-site distance and molecular environment, on the other hand, influence the electrochemistry of the Ru(II) complex as well as the relative rates of electron hopping associated with the Ru(III/II) and Ru(II/I) mixed valent conductive states. Optimum device performance is achieved when balanced charge transport occurs and electrode and self-quenching effects are minimized.

In the first paper of this series,[19] we showed that thin film solid-state light-emitting devices can be successfully fabricated using blends of a small molecule Ru(II) complex dispersed in a matrix of poly(ethylene oxide). Such devices produced luminance levels of about 100 cd/m^2 but operated with low external device efficiencies (about 0.02%). It was further demonstrated that this behavior could be realized without the need of elaborate charging schemes involving the use of elevated temperatures or solvent treatments that enhance ionic conductivity. Devices were fabricated via conventional processing routes and conditioned to high light output with a few simple voltage scans. In this paper, it will be demonstrated that a layer-by-layer molecular-level blending scheme can be used to fabricate thin film devices with external quantum efficiencies in the $1-3\%$ range. In this process, a water-soluble Ru(II)-containing

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Scheme 1. Structures of the Polycations and Polyanions Used for Device Fabrication
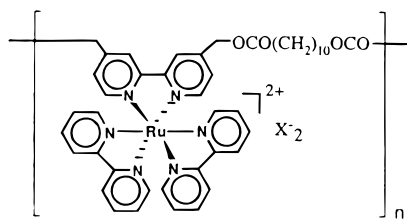
1 Ru(bpy)$_3^{+2}$ polyester (X=Cl$^-$ or PF$_6^-$)
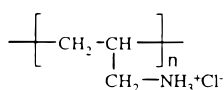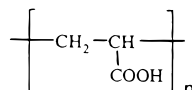
2 poly(allylamine hydrochloride) PAH   **3** poly(acrylic acid) PAA

polyester is used as a polycation in conjunction with the polyanion, poly(acrylic acid), to assemble sequentially adsorbed polyelectrolyte layers. By controlling through pH adjustments the linear charge density of poly(acrylic acid), both as an adsorbing polymer and as a previously adsorbed layer, it is possible to use this approach to systematically control the composition of the resultant thin films, the net result being the ability to create high efficiency thin film devices. Such high quality thin films would not be possible by a simple solution-blending approach as the mixing of a polyanion and a divalent polycation immediately results in the formation an insoluble polymer salt.

Experimental Section

The chemical structure of the Ru(bpy)$_3^{2+}$ polyester is shown in Scheme 1. Details concerning the synthesis and characterization of this polymer can be found in a previous paper.[12] The solubility of the Ru-(bpy)$_3^{2+}$ polyester can be varied by changing the counterion from Cl$^-$ to PF$_6^-$. It is soluble in solvents such as water and methanol in the former case and polar organic solvents such as chloroform, tetrahydrofuran, acetone, and 2-methoxyethanol in the latter case. The number average degree of polymerization of the Ru(bpy)$_3^{2+}$ polyester is estimated to be in the range of 5−10 structural units; i.e., it is essentially an oligomer.

A 2-methoxyethanol solution containing 3% (w/w) Ru(bpy)$_3^{2+}$ polyester (X$^-$ = PF$_6^-$) was used for spin-coating. A water soluble version of the Ru(bpy)$_3^{2+}$ polyester (X$^-$ = Cl$^-$) was used for aqueous sequential adsorption with appropriate polyanions. The polyelectrolytes, poly(allylamine hydrochloride) (PAH; MW = 50 000−65 000) and poly(acrylic acid, sodium salt) (PAA; MW = 50 000, 25% aqueous solution), were commercially available; their structures are shown in Scheme 1. Solutions of these polyelectrolytes were prepared by dissolution in Millipore water to a concentration of 1×10^{-2} M (based on the repeat unit). The pH was then adjusted with HCl to the desired value. Prior to the layer-by-layer adsorption procedure, all solutions were filtered through a 0.45-μm filter. A detailed description of the preparation of the substrates and the basic self-assembly process can be found in our previous papers.[20] In all cases, a single bilayer of PAH and PAA was hand-dipped onto the substrates to improve the multilayer deposition process, starting with the PAH layer. Sequentially adsorbed multi-bilayers of the Ru(bpy)$_3^{2+}$ polyester and PAA were made by alternate dipping of a substrate into solutions of the Ru(bpy)$_3^{2+}$ polyester and the polyanion. This process was carried out using an automatic computer-controlled dipping machine. Following the adsorption of the
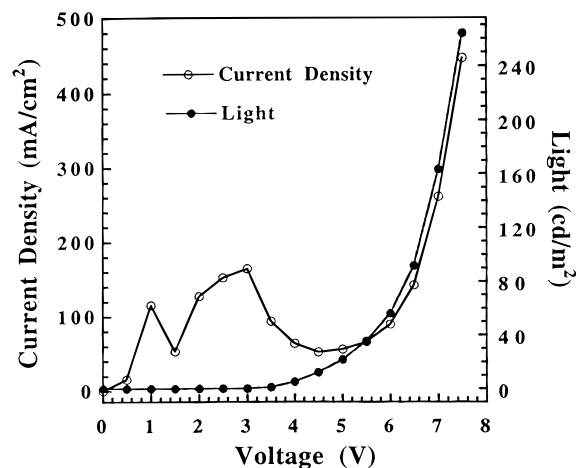
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Figure 1. Current−voltage and light−voltage characteristics of a spin-coated Ru(bpy)$_3^{2+}$ polyester device. The Ru(bpy)$_3^{2+}$ polyester thin film was spin-coated from a 3% (w/w) 2-methoxyethanol solution at 2000 rpm.

polycation or the polyanion, the substrate was rinsed three times with pH-adjusted Millipore water. Thicknesses of the sequentially adsorbed layers were measured by ellipsometry. In all cases, the multilayer thin films ended with PAA as the outermost layer, i.e., the layer in contact with the Al electrode was PAA.

A typical sandwich-structured light-emitting device was fabricated by first depositing or assembling the Ru(bpy)$_3^{2+}$ polyester on a patterned ITO substrate and then thermally evaporating an aluminum electrode on top of the thin film. The intersection of the ITO and the aluminum electrodes gives an active device area of 4 mm^2. The thin films used for device fabrication, including both the spin-coated and sequentially adsorbed multilayers, were thermally treated at 110 °C for 12 h before aluminization. All device measurements were carried out inside a nitrogen glovebox. DC data were collected using a programmed current−voltage and light−voltage setup, which includes a Keithley programmable voltage source, a Hewlett-Packard multimeter, and a calibrated silicon photodiode. AC data were obtained using a programmed light-frequency setup, which includes a Wavelek sweep/function generator and a Hewlett-Packard precision LCR meter. Devices were typically scanned over the voltage range of interest with a step voltage of 0.5 V. The delay time for each step was 5 s at each voltage. External device efficiencies were estimated as described in a previous paper.[19]

Unless otherwise noted, scanned devices were preconditioned by repetitive scanning to increasingly higher voltages (typically two to three scans at each voltage up to the maximum voltage applied). In the step voltage measurements, the devices were preconditioned by first stepping the voltage to reverse bias, returning it to zero bias, and then stepping it to a forward bias with a 5 s hold at each step. This process was repeated two or three times at each voltage (typically starting at 10 V), and the voltage was increased until maximum efficiency was achieved. The turn-on voltage mentioned in this paper is defined as the voltage at which 1 nw of light is detected. Forward bias in this paper simply means that the ITO electrode is biased positive, whereas reverse bias means the aluminum electrode is biased positive.

Results

Spin-Coated Devices. Figure 1 shows a typical current−voltage and luminance−voltage curve obtained from a spin-coated ITO/Ru(bpy)$_3^{2+}$ polyester/Al device (polyester film thickness: ca. 600 Å). This particular device was preconditioned by scanning to 6 V forward bias once. The spin-coated devices of this material exhibit a low turn-on voltage of around 2.5 V, uniformly emit red-orange light and reach a maximum luminance level in the range of 200−300 cd/m^2 at 7.5 V. Devices of this type can be reproducibly driven to 7.0 V with similar results but display a rapid degradation in both current and

luminance at higher voltages. The estimated external quantum efficiency (EQE) of the spin-coated devices is about 0.1−0.2% photons/electron. In the reverse bias (not shown), currents of comparable magnitude are obtained, i.e., the device current response is nearly symmetric about zero bias. The light output in the reverse bias, however, is negligible as was found in our previous studies of a trischelated complex of ruthenium (II) with 4,7-diphenyl-1,10-phenanthroline disulfonate ligands.[19]

The dynamic response of the spin-coated devices is relatively fast. Only one preconditioning scan is needed to obtain reproducible behavior. The current spikes seen at low voltages in the spin-coated devices (see Figure 1) most likely reflect electrode edge effects and other effects related to the thickness nonuniformities that often result from a spin-coating process. Thus, although the spin-coated films exhibit high brightness and respectable device efficiencies, they suffer the usual problems associated with a spin-coating process utilizing a low-molecular weight polymer.

Layer-by-Layer Deposited Devices. To improve film quality and to better control charge injection and transport in devices based on this new Ru(II)-containing polyester, we utilized a layer-by-layer sequential adsorption process to fabricate thin films of this material.[20] To accomplish this goal, a water soluble version of the Ru(bpy)$_3^{+2}$ polyester ($X^- = Cl^-$) was used as the polycation, and poly(acrylic acid) was used as the polyanion. We have previously found that this bilayer combination is capable of producing devices with the highest quantum efficiency.[14] In all cases, a single bilayer of PAH/PAA was deposited onto the patterned ITO glass substrates prior to the deposition of the Ru(bpy)$_3^{+2}$ polyester/PAA multilayers (starting with PAH as the first deposited layer, total bilayer thickness estimated to be in the 10−20 Å range). This initial "prep" bilayer of PAH/PAA is used to promote uniform film deposition of the Ru(bpy)$_3^{2+}$ polyester/PAA multilayers.

Our previous fundamental studies carried out with weak polyacids such as PAA have shown that it is possible to systematically control the thickness contributed by each layer, the bilayer composition, and the level of layer interpenetration established in a sequential adsorption process by simply adjusting the pH of the polymer dipping solutions. Through this type of control, it is possible to blend, at the molecular level, the two polyelectrolytes used to fabricate the multilayer thin films. Details concerning how this process works can be found in a previous paper.[21]

To determine the influence of solution pH on the multilayer deposition of the sequentially adsorbed Ru(bpy)$_3^{2+}$ polyester/PAA system, we carried out multilayer assembly by using dipping solutions with different pH levels. For this purpose, the concentration of all solutions was maintained at 0.01 M, and no salt or buffer was added to any of the dipping solutions. The pH of the rinsing water was adjusted to the same pH as that of the previous dipping solution. Two different deposition strategies were explored. In one case, the pH of the Ru(bpy)$_3^{2+}$ polyester solution was held constant at 3.5, and the pH of the PAA solution was varied from 2.5 to 4.5. In the other case, the pH of the PAA solution was held constant at 3.5, and the pH of the Ru(bpy)$_3^{2+}$ polyester solution was varied from 2.5 to 4.5. A linear relationship between thickness and the number of deposited bilayers was observed for all of these different deposition conditions (typically measured on films with from 6 to 12 bilayers).[13] Figure 2 shows the average layer thickness contribution made by the Ru(bpy)$_3^{2+}$ polyester and PAA to the basic bilayer building block of the multilayer thin films for these
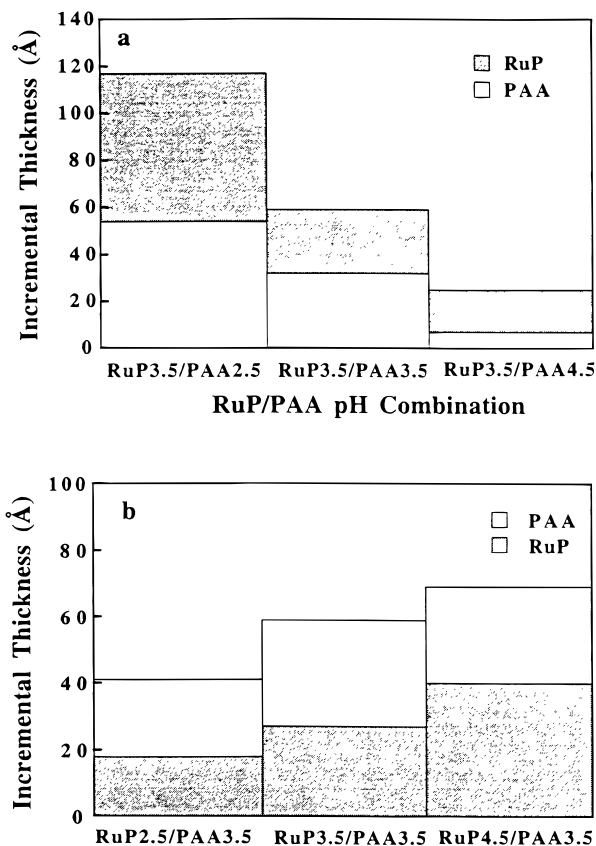
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Figure 2. pH dependence of the average layer thickness contribution of the Ru(bpy)$_3^{2+}$ polyester and PAA to the bilayer building block (measured on films after drying at 100 °C for 2 h).

various processing conditions. It should be noted that the polycation and polyanion layers of these sequentially adsorbed films are typically highly interpenetrated.[21] The data presented in Figure 2 simply show the increase in thickness that occurs when a polymer layer is adsorbed onto a multilayer film and the film is dried. For the purposes of this paper, this figure provides information about the composition (relative amounts of Ru(bpy)$_3^{2+}$ polyester and PAA) of the bilayer building block used to fabricate the multilayer thin film devices, and it should be assumed that the two layers (polycation and polyanion) are homogeneously mixed.

As can be seen in Figure 2, the thickness contribution of the polycation and polyanion layer can be systematically controlled via manipulation of dipping solution pH, thereby providing a means to control the relative amount of Ru(bpy)$_3^{2+}$ polyester that is incorporated in the bilayer building block (verified with optical spectroscopy). In all cases, the resultant multilayer thin films are exceptionally uniform and exhibit an absorption and photoluminescence band centered at 460 and 630 nm, respectively, both associated with the metal−ligand charge-transfer band (MLCT) band of the Ru(bpy)$_3^{+2}$ polyester.

Figure 3 shows how bilayer composition influences the device performance of the sequentially adsorbed multilayer films. Four different bilayer compositions were examined in detail with Ru-(bpy)$_3^{2+}$ polyester thickness contributions of 46, 58, 70, and 80%. The pH conditions used to create these four different bilayer compositions were RuP 3.5/PAA 3.5, RuP 4.5/PAA 3.5, RuP 3.5/PAA 4.5, and RuP 4.5/PAA 4.5, respectively. To eliminate thickness effects, the total thickness of all of the Ru-(bpy)$_3^{2+}$ polyester/PAA multilayers used in these particular devices was set to about 1100 Å. In this case, devices were tested using the step voltage procedure described in the
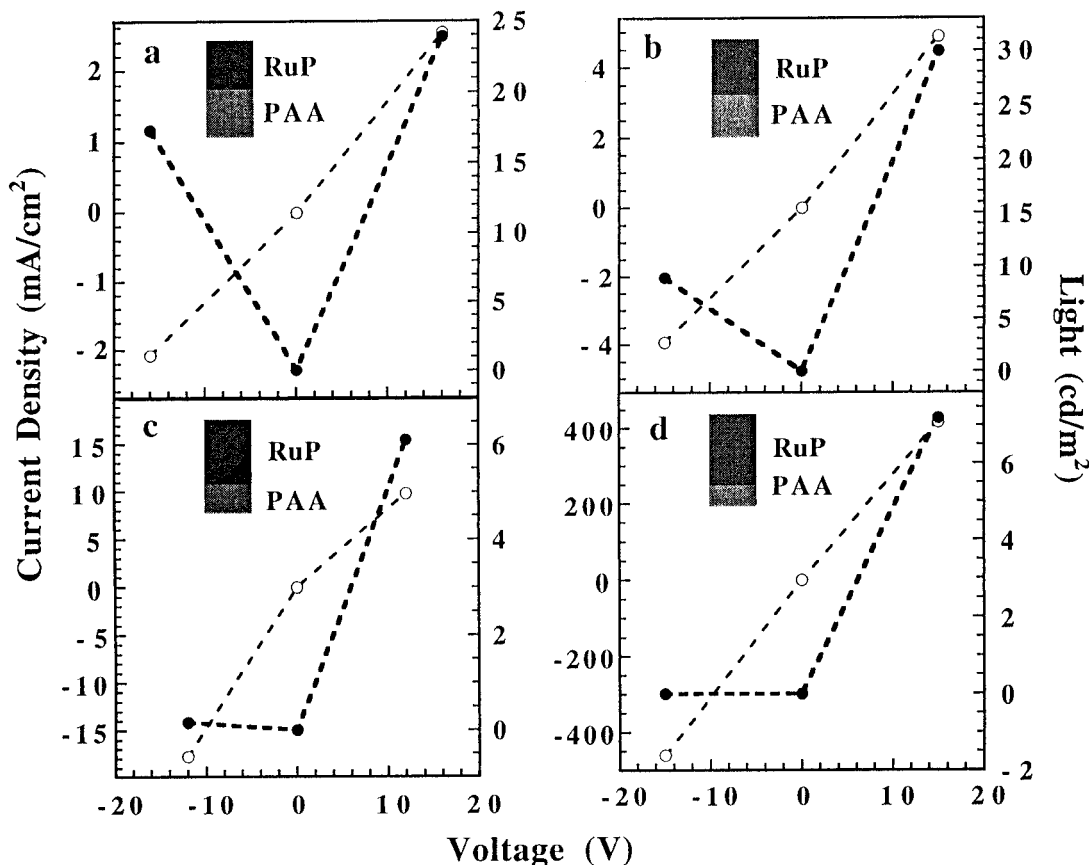
Figure 3. Current−voltage and light−voltage characteristics of devices based on sequentially adsorbed layers of Ru(bpy)$_3^{2+}$ polyester and PAA with different bilayer compositions. Open circles represent current density, and solid circles represent light. Devices were tested with the step voltage method, dotted lines are only present to aide the eye. (a) 46% Ru(bpy)$_3^{2+}$ polyester (deposition conditions: RuP 3.5/PAA 3.5); (b) 58% Ru(bpy)$_3^{2+}$ polyester (deposition conditions: RuP 4.5/PAA 3.5); (c) 70% Ru(bpy)$_3^{2+}$ polyester (deposition conditions: RuP 3.5/PAA 4.5); (d) 80% Ru(bpy)$_3^{2+}$ polyester (deposition conditions: RuP 4.5/PAA 4.5).

Table 1. Device Performance of Multilayer Films Measured by Step Voltage Method

device	% thickness contribution to bilayer[a]	forward bias (ITO as Anode)		reverse bias (Al as Anode)	
		light cd/m^2	% external efficiency	light cd/m^2	% external efficiency
RuP 3.5/PAA 3.5	46	25	3.0	17	3.0
RuP 4.5/PAA 3.5	58	30	2.0	9	1.0
RuP 3.5/PAA 4.5	70	6	0.2	0.2	0.006
RuP 4.5/PAA 4.5	80	7	0.006		
spin coating[b]	100	265	0.2		

[a] Represents thickness contribution of the Ru(bpy)$_3^{2+}$ polyester to the bilayer building block. [b] Spin coated from a 2-methoxyethanol solution containing 3% (w/w) Ru(bpy)$_3^{2+}$ polyester (X$^-$ = PF$_6^-$).

Experimental Section. This procedure makes it possible to push the devices to higher voltages and provides useful information about the dynamics of the device response.

As indicated in Figure 3, the performance of the self-assembled devices is dramatically dependent on the Ru(bpy)$_3^{2+}$ polyester contribution to the bilayer building block. As the Ru-(bpy)$_3^{2+}$ polyester composition decreases from 80 to 46%, the external device efficiency increases from 0.006 to about 3.0% and the maximum luminance level obtained increases from 7 to 25 cd/m^2 (see Table 1). Also note that the reverse bias behavior changes remarkably over this compositional range. At the highest Ru(bpy)$_3^{2+}$ polyester composition, the devices are asymmetric, only producing light in the forward bias; however, as the PAA contribution to the bilayer increases, the devices become more symmetric and eventually achieve nearly complete

symmetric behavior (46% case) with comparable luminance levels and efficiencies in both the forward and reverse bias. The high external efficiencies of these latter devices (consistently in the 2−3% range) are comparable to the best devices reported for either conjugated polymer or small-molecule organic-based devices.[22] The high efficiencies of the Ru(bpy)$_3^{2+}$ polyester multilayer devices, however, are realized without the need to use relatively unstable, low work function metals such as magnesium and calcium as is typically required with these other systems.

Figure 4 shows the typical current−voltage and luminance−voltage characteristics obtained from an ITO/(PAH/PAA)$_1$/(Ru-(bpy)$_3^{2+}$ polyester/PAA)$_{20}$)/Al device (total device thickness: 1100 Å) fabricated with the 46% Ru(bpy)$_3^{2+}$ polyester bilayer building block. In this case, the forward and reverse bias data were obtained from separate cells after preconditioning the devices by scanning to 8 and 10 V successively in forward bias or −8 and −10 V in reverse bias. This particular device turned on at about 6.5−7 V forward bias and reached a maximum luminance level of 7 cd/m^2 with an external quantum efficiency of about 2%. The nearly symmetric device behavior observed in the step voltage experiment is also observed in this more conventional scanning mode. To date, we have fabricated more than 100 devices of this type and found them all to produce

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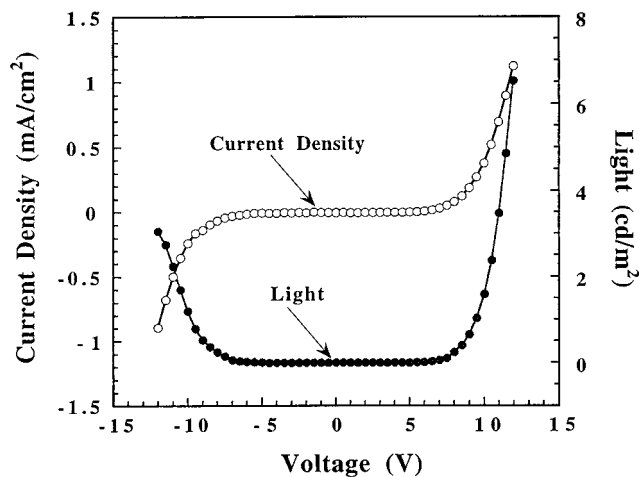
Figure 4. Current−voltage and light−voltage characteristics of a device composed of 20 bilayers of the 46% Ru(bpy)$_3^{2+}$ polyester system.

nearly identical performance when probed in this fashion, i.e., about 2% external quantum efficiency, up to 10 cd/m^2 maximum luminance and essentially symmetric device behavior. Compared to the spin-coated films of this material, the compositionally optimized devices based on the sequentially adsorbed Ru-(bpy)$_3^{2+}$ polyester/PAA multilayers turn on at higher voltages, exhibit much "cleaner" current−voltage scans, support significantly lower current densities, reach lower maximum luminance levels, exhibit essentially symmetric light output, and are about an order of magnitude more efficient.

To understand why the devices fabricated from sequentially adsorbed polyion layers turn on at higher voltages than the spin-coated devices we examined their thickness-dependent device characteristics. This is readily carried out with a molecular-level layer-by-layer processing approach as the thickness of the resultant multilayer film is determined with a high degree of precision simply by the number of deposited layers. Three 46% Ru(bpy)$_3^{2+}$ polyester multilayer devices with 15, 25, and 35 Ru(bpy)$_3^{2+}$ polyester/PAA bilayers, corresponding to thicknesses of 885, 1475, and 2065 Å respectively, were fabricated and examined. A strong film thickness dependence was clearly observed (data not shown): the turn-on voltage was found to shift from about 3 (15 bilayers) to about 10 V (35 bilayers) with increasing film thickness. In addition, the total light output in the forward bias was found to increase with decreasing film thickness (the maximum forward bias luminance level of the 15-bilayer film was about 3 times that of the 35-bilayer film) while the reverse bias light output remained about the same. The device efficiency, on the other hand, was found to decrease from over 2 (35 bilayers) to about 0.2% (15 bilayers) as film thickness decreased. The thickness dependent behavior of the Ru(bpy)$_3^{2+}$ polyester/PAA multilayer films indicates that the device turn-on voltage is controlled by the bulk resistance of the multilayer film (to be discussed).

To study the dynamic response of devices fabricated from the multilayer thin films, we examined the light/current characteristics of devices scanned from forward to reverse bias and from reverse to forward bias without any prior conditioning. A 35-bilayer, 46% Ru(bpy)$_3^{2+}$ polyester device (film thickness: 2065 Å) was used for this study. Figure 5a shows the case where a voltage was applied in the forward bias first, followed by a sweep to the reverse bias. Figure 5b, on the other hand, shows the case where the voltage was applied first in the reverse bias and subsequently swept to the forward bias. In both cases, it can be seen that a distinct "charging" hysteresis is observed in
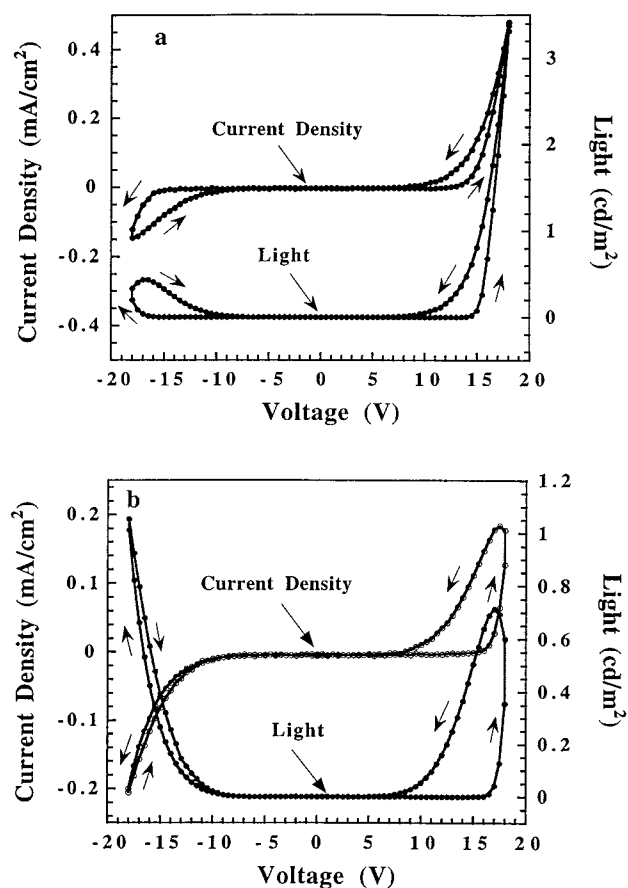

Figure 5. Current−voltage and light−voltage curves of a device composed of 35 bilayers of the 46% Ru(bpy)$_3^{2+}$ polyester system. (a) Device was scanned in the forward bias first, then in the reverse bias. (b) Device was scanned in the reverse bias first, then in the forward bias.

the form of an increase in light output and current as the device returns to zero bias from its highest applied voltage. When driven to the forward bias first, very little light or current is observed during the first reverse bias sweep. Only if this same device is repeatedly driven to the reverse bias will it develop its maximum possible light output and current density. For a device first driven to the reverse bias, a higher current density and light output are realized, as well as a pronounced hysteresis during the first scan to the forward bias. Again, it requires multiple scans, in this case in the forward bias, to achieve the maximum possible light output observed in the forward bias. This distinct charging behavior is consistent with an electrochemical mechanism of charge injection and transport in which serial concentration gradients of Ru(II)/(III) and Ru(I)/(II) redox couples are formed at the anode and cathode side of the device, respectively.[17,18] The hysteresis and charging effects observed during subsequent voltage scans to the opposite bias reflect the dynamics of reversing the serial concentration gradients established during the first voltage scan.

The sluggish dynamic response of these devices would seem to indicate that it is not possible to drive a device of this type with an AC field. We have found, however, that with the proper conditioning, applied voltage, and film thickness, the nearly symmetric device characteristics of the 46% Ru(bpy)$_3^{2+}$ polyester multilayer system can in fact be exploited to create AC-driven devices. This was accomplished in the following manner. The device was preconditioned by stepping the voltage first to a reverse bias, back to zero bias, and then to a similar forward bias (with a 5 s hold at each step). This process was repeated
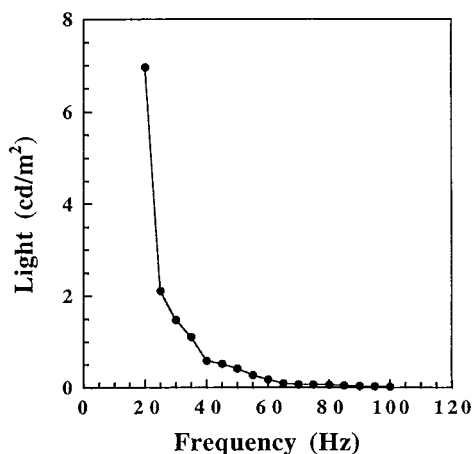
Figure 6. AC response of a device composed of 20 bilayers of the 46% $Ru(bpy)_3^{2+}$ polyester system operated with a sinusoidal 20 V peak-to-peak AC voltage. See paper for details concerning device preconditioning.

two to three times at each voltage. The step voltage was initially set at 10 V and was incrementally increased to 16 V. Figure 6 shows the frequency-dependent response of a 20-bilayer device that was conditioned in this manner and subsequently driven with a sinusoidal 20 V peak-to-peak AC voltage. At 20 Hz, the device can be successfully operated in AC mode (with light emission in both forward and reverse bias) at a luminance level of about 7 cd/m². With increasing frequency, it can be seen that the light output decreases dramatically, eventually going below the detection limit of our photodiode at about 90 Hz. This frequency response is completely reversible; i.e., similar light levels are obtained when the device frequency is dropped back to 20 Hz.

Multilayer Heterostructures: Compositionally Graded Devices and Interface Modification. The use of a layer-by-layer processing scheme makes it possible to fabricate more complex, compositionally graded structures in which the amount of the $Ru(bpy)_3^{2+}$ polyester in the bilayer is varied across the multilayer thin film. Such structures provide useful insight into the mechanism of device operation and provide an opportunity to further optimize the performance of these devices. Figure 7 shows the device characteristics obtained from two compositionally graded devices fabricated with 10 bilayers of the 46% $Ru(bpy)_3^{2+}$ polyester bilayer system and 25 bilayers of the 80% $Ru(bpy)_3^{2+}$ polyester bilayer system. In one case (Figure 7a), the 10-bilayer block was placed next to the ITO electrode, whereas in the other (Figure 7b), it was placed next to the aluminum electrode. The total thickness of each multilayer heterostructure was about 1100 Å with approximately an equal thickness being contributed by each bilayer system (550 Å). Devices were tested by both the scanning method and the step voltage method (data in figure inset) and were preconditioned as described in the Experimental section.

These results show that with suitable compositional grading of the multilayer structure it is possible to fabricate devices that can be driven to higher luminance levels (as high as 50 cd/m² in the step voltage mode) and, most interestingly, to create devices that emit light either only in the forward bias or only in the reverse bias. For example, in the step voltage mode of testing, the device fabricated with the 10 bilayers of the 46% $Ru(bpy)_3^{2+}$ polyester bilayer system next to the ITO electrode emits light only in the forward bias, whereas the device fabricated with these 10 bilayers next to the Al electrode only emits light in the reverse bias. In the scanning testing mode, both devices exhibit highly rectifying current−voltage behavior
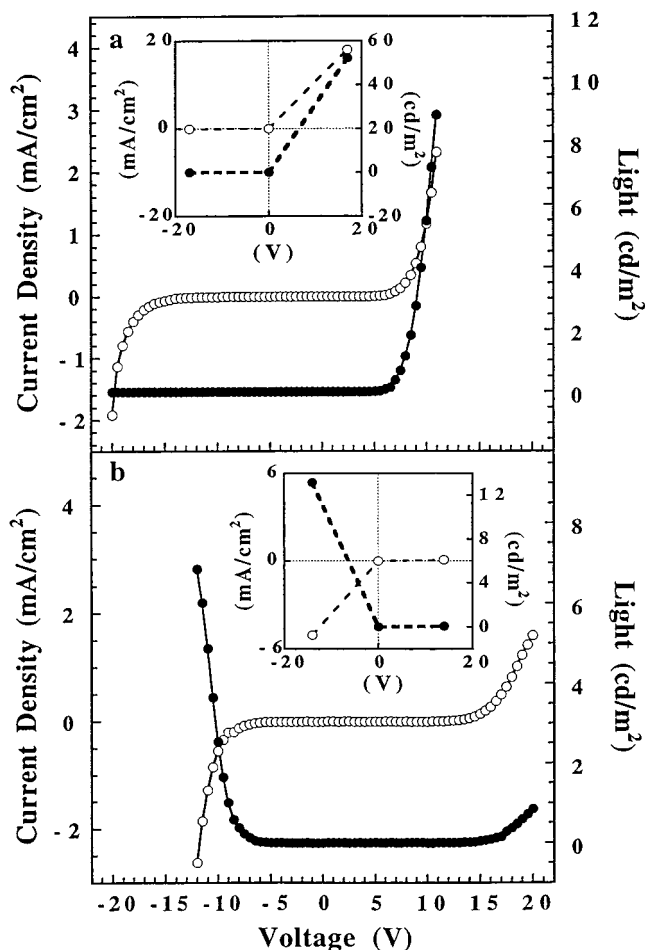

Figure 7. Device performance of compositionally graded devices; (a) ITO/(RuP 46%)₁₀/(RuP 80%)₂₅/Al; (b) ITO/(RuP 80%)₂₅/(RuP 46%)₁₀/Al. Inset shows the step voltage behavior of the device. Open circles represent current density and solid circles represent light.

over the −12 to +12 V range. Only when these devices are driven in the opposite bias to voltages much higher than that required to create light in their respective light-emitting biases is significant current flow observed to occur. This is in sharp contrast to devices fabricated solely from the 46% $Ru(bpy)_3^{2+}$ polyester bilayer system in which the current−voltage behavior is found to be nearly symmetrical (see Figure 4). The external quantum efficiency determined from the step voltage experiments for both of the compositionally graded heterostructures was determined to be about 0.7% in the bias of light output. The efficiency of these devices as well as the magnitude of their maximum current densities are controlled primarily by the more resistant and efficient 46% $Ru(bpy)_3^{2+}$ polyester bilayer system. Recall that devices based on the 80% $Ru(bpy)_3^{2+}$ polyester bilayer system exhibit very high current densities and low efficiency (ca. 0.006%, see Figure 3d).

We have also found that it is possible to control device behavior via the use of thin insulating layers placed at either the anode or cathode interface. This was accomplished with the use of insulating bilayers of PAH/PAA in combination with multilayers of the 46% $Ru(bpy)_3^{2+}$ polyester/PAA bilayer system. Figure 8 shows the step voltage device characteristics obtained from multilayer heterostructure films containing 20 bilayers of the 46% $Ru(bpy)_3^{2+}$ polyester/PAA bilayer system (1100 Å) and three additional bilayers of PAH/PAA (about 90 Å total thickness) at either the cathode, anode or both interfaces Note that all of the multilayer films examined in this work are
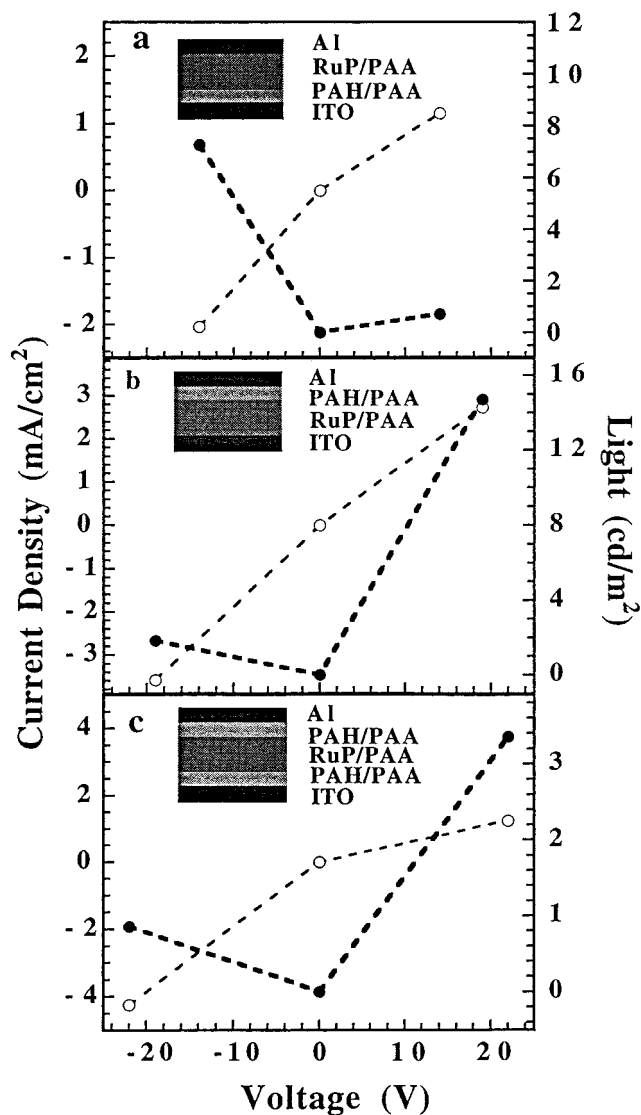
Figure 8. Device performance the 46% $Ru(bpy)_3^{2+}$ polyester system with insulating layers at different electrode interfaces. (a) $ITO/(PAH/PAA)_4/(RuP/PAA)_{20}/Al$; (b) $ITO/(PAH/PAA)_1/(RuP/PAA)_{20}/(PAH/PAA)_3/Al$; (c) $ITO/(PAH/PAA)_4/(RuP/PAA)_{20}/(PAH/PAA)_3/Al$. Open circles represent current density and solid circles represent light.

started with a "prep" bilayer of PAH/PAA at the ITO electrode. Thus, when the three bilayers of PAH/PAA are added to the ITO interface, the total number of bilayers at this interface is actually four.

As indicated in Figure 8a and b, when the thin insulating bilayers are present at an electrode acting as the anode (ITO in forward bias, Al in reverse bias), the maximum luminance level of the device is significantly diminished compared to similar devices without the insulating layers. Recall that the 46% Ru-$(bpy)_3^{2+}$ polyester/PAA bilayer system without the additional insulating layers can be driven symmetrically in the step voltage mode to maximum luminance levels in the $15-25$ cd/m^2 range. Much less of an effect is observed when the electrode with the insulating bilayers is biased as the cathode of the device. When insulating layers are present at both electrodes (Figure 8c), the maximum light output in the forward bias (ITO as the anode) recovers a bit (from about 1 to 3.5 cd/m^2) relative to the device with insulating layers only at the ITO interface, whereas the maximum light output possible in the reverse bias (Al as the anode) decreases slightly relative to the device with insulating layers only at the Al interface. Thus, the nearly symmetric device

behavior of the 46% $Ru(bpy)_3^{2+}$ polyester/PAA bilayer system can be rendered asymmetric, with higher light output in either the forward or the reverse bias, by placing insulating layers at the appropriate electrode.

Interestingly, the placement of insulating layers at either the ITO or Al interface does not appear to significantly influence the maximum current densities possible in these devices: current densities in the $1-3$ mA/cm^2 range are observed with or without the added insulating layers. The presence of insulating layers does, however, decrease the maximum external device efficiency possible from this bilayer system from about 3.0 to about 1.0%. Overall, these results show that thin insulating layers have more of an effect on the oxidation process of the Ru(II) complex than on the reduction process. More detailed studies are currently underway to determine the origin of these interesting compositional grading and insulating layer effects.

Large Area Devices and Flexible Devices. An advantage of using a layer-by-layer deposition technique involving the sequential adsorption of polyelectrolytes is that it is possible to easily fabricate large area devices with uniform film thickness on virtually any type of substrate. To demonstrate this, we fabricated devices with active areas of 60 mm^2, an area 15 times larger than the devices described above. These devices were consistently found to produce red-orange light uniformly over the entire device area without any defects or inactive device area. The external quantum efficiency and light output of these devices were identical to that found with the smaller devices (i.e., about 25 cd/m^2 at $2-3$% external efficiency). We anticipate that much larger device areas are readily possible with this processing approach. Such large area, uniformly emitting devices of this material would be very difficult to create using conventional spin-coating methods.

We have also used this approach to fabricate flexible light-emitting devices. These devices were fabricated by depositing the $Ru(bpy)_3^{2+}$ polyester/PAA multilayers onto flexible poly-(ethylene terephthalate) sheets that were patterned with electrically conductive polypyrrole electrodes.[23] The devices were completed via the deposition of aluminum electrodes to create active device areas of 2×10 mm^2. Similar device performance was also found with these devices even with the use of polypyrrole as the anode or cathode.

Discussion

The electrochemical generation of light from solutions of the Ru(II) complex is a well-known and extensively studied phenomenon.[1−10] The understanding and techniques needed to fabricate solid-state Ru(II)-based light-emitting devices of comparable efficiency and brightness, however, have only recently started to emerge.[11−19] Critical issues related to the realization of high efficiency, solid-state devices driven by an electrochemical mechanism of charge injection and transport include: (1) the successful creation of the Ru(III) and Ru(I) species at the anode and cathode respectively and (2) the balanced redox transport of these species away from their respective electrodes to allow them to undergo the annihilation reaction needed to produce the light-emitting Ru(II)* excited state. Recent studies[17,18] have revealed that solid-state redox conduction in these materials is facilitated by the formation of serial concentration gradients of Ru(III/II) and Ru(II/I) couples, ultimately leading to a voltage-gradient driven charge transport process. Thus, to activate the electrochemistry of the Ru(II) complex, it is necessary to design thin films that support some level of ionic conductivity. Control over the average site-to-

(23) Results to be submitted for publication.

site distance of the Ru(II) complexes is also desirable as it provides a means to reduce self-quenching effects and to influence electron-transfer rates (between the Ru(II) complexes and between the electrodes and the Ru(II) complexes).

In the multilayer thin films described in this paper, a cationic Ru(II) containing polyester is blended with the polyanion, poly-(acrylic acid), via a layer-by-layer sequential adsorption process. Due to the high level of molecular interpenetration that occurs between the polycation and polyanion in this process, the resultant thin films are best considered as an essentially homogeneous blend of the two polyelectrolytes.[21] As indicated in the Results, the composition of these thin film blends can be systematically varied by simple adjustments of the pH of the dipping solutions. This, in turn, makes it possible to control the average site-to-site distance of the electrochemically active Ru(II) complexes as well as to modify the local molecular environment of these entities. The average site-to-site distance of the Ru(II) complexes determines the rates of redox conduction facilitated by the Ru(III/II) and Ru(II/I) couples as well as self-quenching rates. The local molecular environment of the Ru-(II) complex, on the other hand, influences its electrochemistry.

Devices based on nonblended films of the Ru(bpy)$_3^{2+}$ polyester (spin-coated films) exhibit high luminance levels but only modest efficiencies (0.1−0.2% EQE). In addition, symmetric current flow but no light is detected during reverse bias operation. In the sequentially adsorbed films, device efficiency systematically increases as the amount of Ru(bpy)$_3^{2+}$ polyester incorporated in the bilayer building block is reduced, reaching levels as high as 3% in the film composition containing 46% Ru(bpy)$_3^{2+}$ polyester. This dramatic improvement in device efficiency, in part, is associated with a reduction in self-quenching effects. Measurements of the photoluminescence intensity of thin films of comparable thickness and optical absorption (measurements were made under identical conditions and thus provide a relative ranking of the photoluminescence intensity of different films) indicate that the highest efficiency multilayer devices (1−3%) are about 7 to 9 times more photoluminescent than films of the spin-coated Ru(bpy)$_3^{2+}$ polyester. Thus, dilution of the Ru(II) complexes in a polyelectrolyte matrix clearly enhances the photoluminescence of these films which, in turn, appears to result in improved device efficiencies. It is unclear at the moment if other factors associated with modifications of the charge injection and transport processes active in these films are also playing an important role in the observed improvements in device efficiency. In an attempt to identify how these other factors might contribute to the improved device efficiency of the multilayer films, we are currently examining their temperature and frequency-dependent transport properties.

Dilution of the Ru(II) complex in a matrix of poly(acrylic acid) clearly enhances device efficiency, but it also significantly increases the bulk resistance of the film and lowers its maximum possible light output. In addition, relatively high voltages must be used to drive the device, and there is a distinct thickness dependence of the turn-on voltage (increases with increasing film thickness). This is to be contrasted with devices based on the spin-coated film of the Ru(bpy)$_3^{2+}$ polyester and other small-molecule Ru(II) complexes we have examined that display low turn-on voltages (typically in the 2.5−3 V range) and a thickness-independent turn-on voltage for films in the 500−2000 Å thickness range.

The higher operating voltages and lower luminance levels that we have generally found with devices based on sequentially adsorbed films containing the Ru(II) complex, in part, reflect the very low ionic conductivity of these films. During the sequential adsorption process, most of the small ions associated with the polyanion and polycation (Na$^+$ and Cl$^-$, respectively) are entropically displaced in favor of polymer−polymer contact ion pairs. The net result is a highly interpenetrated and ionically cross-linked polyelectrolyte matrix with a relatively low concentration of small ions (presumably of low ionic mobility). Preliminary measurements of the room-temperature DC ionic conductivity (determined by impedance measurements) of the multilayer thin films indicate that they are about 3 orders of magnitude less conductive than thin films cast from small-molecule Ru(II) complexes. Our most efficient multilayer thin films, for example, exhibit a DC conductivity of about 10^{-11} S/cm compared to a value of about 10^{-8} S/cm for a small molecule Ru(bpy)$_3$−diol that we are currently investigating. Thin film devices fabricated from this latter material can be operated at voltages in the 2.5−5.0 V range producing luminance levels as high 1000 cd/m^2.[24] Thus, the operating voltages of more ionically conductive thin films are significantly lower, and their luminance levels significantly higher than what is possible with the polyelectrolyte multilayer films.

The ionic conductivity of the multilayer thin films is clearly not completely quenched as this would inhibit the formation of the Ru(II/III)/Ru(I/II) mixed concentration gradients that are needed to support redox conduction and produce the light-emitting Ru(II) excited state. High operating voltages, however, are needed to overcome the low ionic conductivity of the sequentially adsorbed films and thereby establish the mixed redox gradients of the Ru(II) complex. The large electric fields established in these thin films in the 10−20 V range (>MV/cm) are apparently sufficient to support the levels of ionic conductivity needed to electrochemically activate the Ru(II) complex. Interestingly, it appears that at sufficiently high voltages, the mixed concentration gradients can be reversed (46% Ru(bpy)$_3^{2+}$ polyester system) when a device is alternately stepped from forward to reverse bias. The fact that comparable current densities are observed in both forward and reverse bias (see Figure 3) indicates that the gradient is in fact reversing as opposed to the alternate creation of Ru^{3+} and Ru$^+$ species at the same electrode. AC measurements show that the ionic conductivity needed to support the reversal of the mixed concentration gradient is present up to about 60 Hz, above which point the electric field is oscillating too fast for the ions to respond and the device eventually ceases to operate. This relatively low-frequency cutoff is consistent with a process that is limited by ionic conductivity.

It remains to be determined just how redox gradients of the type described by Wightman and co-workers[17,18] are being established in our multilayer thin films. Given the fact the anions and cations present in these films are primarily polymeric in nature and therefore immobile, the question remains as to what mobile ionic entities are facilitating the counterion redistribution that is required to maintain charge neutrality. In addition to the low level of small ions that are inevitably present in these films, it is also possible that protons from the nonionized carboxylic acid groups of PAA are fulfilling this role. We estimate via FTIR spectroscopy that only about 50−60% of the acid groups of PAA are being utilized to construct a multilayer thin film at a pH of 3.5, leaving the remaining nonionized acid groups as potential donors of mobile protonic cations. Recently, Neher et al.[25] have demonstrated that thin film devices based on a

(24) Handy, E.; Pal, A.; Rubner, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 3525.

(25) Neher, D.; Gruner, J.; Cimrova, V.; Schmidt, W.; Rulkens, R.; Lauter, U. *Polym. Adv. Technol.* **1998**, *9*, 461.

luminescent sulfonated poly(*p*-phenylene) operate as light-emitting electrochemical cells (LEC) in which mobile protons or sodium ions serve to establish ionic double layers at the electrode interfaces and to provide the counterions needed to facilitate the electrochemical doping process. The DC conductivity of films of this rigid-rod polyelectrolyte is about 10^{-11} S/cm, a value very similar to what we find for our most efficient multilayer thin film. These authors argue that the current densities of such devices can be influenced by both bulk transport-limited and interface-limited charge transport behaviors, depending on the width of the ionic double layer present at the interfaces. Thus, a less than optimum ionic conductivity can also raise the operating voltage of a device due to the establishment of poorly developed ionic space charge layers at the interfaces. Clearly, there are many factors at play in light-emitting devices driven by electrochemical processes.

As mentioned earlier, devices based on films of the spin-coated $Ru(bpy)_3^{2+}$ polyester and in fact all devices that we have examined that utilize neat films of a Ru(II) complex and aluminum electrodes, exhibit symmetrical device behavior with regard to current density but little or no light emission in reverse bias. When a platinum electrode is used to fabricate these same devices in place of aluminum, completely symmetrical current and light characteristics are observed (comparable light output and current density in both the forward and reverse bias). Little or no light emission is observed in the reverse bias with aluminum electrodes due to the fact that when the aluminum electrode is biased as the anode $(+)$, it is apparently more easily oxidized than the Ru(II) complex. The net result is that the Ru-(II/III) redox couple that is needed to generate light emission is not readily formed in the device.

With the $Ru(bpy)_3^{2+}$ polyester/PAA system, devices with increasingly symmetrical light characteristics are obtained as the composition of the $Ru(bpy)_3^{2+}$ polyester is reduced (see Figure 3). Recall that devices based on the 46% $Ru(bpy)_3^{2+}$ polyester bilayer produce nearly comparable luminance levels in both the forward and reverse bias. This is an interesting observation, considering that all of these devices utilize an aluminum electrode. It appears that the carboxylic acid/carboxylate groups of PAA that are present at the aluminum interface are capable of modifying the electrochemistry of the aluminum electrode in such a manner that it is now possible to effectively oxidize the Ru(II) complex. Although we have yet to determine the exact origin of this effect, it seems reasonable to propose that the carboxylic acid groups are modifying the redox potential of the electrochemically active aluminum that is present at the interface (aluminum oxide is also most definitely present at this interface). The acid groups could be forming aluminum complexes via a chelation-type of interaction. Such interactions would be expected to modify the redox potential of a metal such as aluminum.

It is clear that this is predominately an interface-related effect involving PAA for the following reasons. First, the amount of reverse bias light output increases as the PAA composition of the bilayer building block increases. Even more importantly, we have found that if the outermost layer of a film fabricated from the 46% $Ru(bpy)_3^{2+}$ polyester is the Ru(II) polyester as opposed to PAA, the amount of light produced in the reverse bias decreases compared to what is observed when PAA is the outermost layer. Even though the layers of these sequentially adsorbed films are highly interpenetrated, we have found that the surface of a multilayer film is often enriched in the functional groups of the outermost layer.[21] Hence, when the Ru(II) polyester is the outermost layer of a device, one would expect fewer carboxylic acid groups at the aluminum interface. Second, in the compositionally graded films described in this paper, light emission in the reverse bias is only observed when the PAA rich bilayer (46% $Ru(bpy)_3^{2+}$ polyester) is in contact with the aluminum electrode. Third, the placement of only three bilayers of poly(styrene sulfonic acid)/ $Ru(bpy)_3^{2+}$ polyester on top of a 20-bilayer film of the 46% $Ru(bpy)_3^{2+}$ polyester/PAA system completely quenches the reverse bias light output without changing any of the forward bias device characteristics such as efficiency and current density.[23] When these same three bilayers are placed next to the ITO electrode, no change in reverse bias device behavior is observed, i.e., the device remains symmetrical in light output. Devices fabricated solely from the poly(styrene sulfonic acid)/ $Ru(bpy)_3^{2+}$ polyester bilayer system exhibit no light output when driven to reverse bias.[14] Clearly, the presence of a high concentration of PAA at the aluminum interface dramatically alters the reverse bias behavior of devices based on the Ru(II) complex.

Conclusions

We have demonstrated that the $Ru(bpy)_3^{2+}$ polyester can be used in conjunction with a sequential adsorption process to fabricate highly efficient solid-state light-emitting devices. External quantum efficiencies in the $1-3\%$ range were obtained by simply controlling the composition of the $Ru(bpy)_3^{2+}$ polyester/PAA bilayer building block used to construct the devices. The ability to readily modify interfaces with this new self-assembly approach has also made it possible to create devices that are completely symmetric in light and current or that only emit light in the forward or reverse bias. Such studies have provided new insights into our understanding of the mechanisms of charge injection and transport operating in these electrochemically driven systems.