

Solid-State Light-Emitting Devices Based on the Tris-Chelated Ruthenium(II) Complex. 2. Tris(bipyridyl)ruthenium(II) as a High-Brightness Emitter

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Abstract: We report high-brightness, high-efficiency, solid-state light-emitting devices based on small-molecule Ru(bpy)₃(PF₆)₂ and its derivatives. These devices operate at low voltage (as low as 2.5 V), suggesting a close parallel with well-documented liquid electrogenerated chemiluminescence cells. We have realized luminance levels as high as 1000 cd/m² at only 5 V with spin-cast films and 200 cd/m² at 3 V. Emitted light is red or red-orange in color. At low voltage, external quantum efficiencies on the order of 1% are attainable. Luminance levels and efficiencies of these magnitudes are unprecedented in solid-state Ru(bpy)₃²⁺-based devices. A significant time delay is observed between voltage application and device response, as previously reported. We find that the low-voltage time delay can be circumvented using an initial high-voltage pulse, affording nearly instantaneous high brightness.

1. Introduction

The bipyridyl and phenanthroline complexes of ruthenium(II), extensively studied in liquid electrogenerated chemiluminescence (ECL) cells,^{1–10} have recently come to the fore as solid-state light-emitters.^{11–20} High brightness and efficiency (5–25%) have been realized with liquid ECL cells, and it is expected that similar performance should be possible with solid-state devices, as well, at low voltages. Several workers have demonstrated that an electrochemical mechanism is operative in solid-state devices based on RuL₃²⁺ (L = 2,2'-bipyridine, bpy, or 1,10-phenanthroline, phen, etc.), as originally proposed

by Tokel and Bard for liquid cells.¹ In the solid state, a characteristic feature of this mechanism is a delay (on the order of seconds to minutes) between application of a potential bias and device response.¹¹ This “charging” phenomenon is associated with relatively slow counterion redistribution. Ion redistribution is required in order to establish the mixed-valent redox states needed for charge transport and light emission.^{13,14} If the “charging” time (time to maximum brightness) were shortened, solid-state devices could be considered more seriously for use in practical flat-panel displays. To this end, Maness et al. have reported instantaneous operation from polymeric Ru(bpy)₃²⁺-based films that had been “precharged” (while solvent-swollen or at elevated temperature), but such preconditioned devices produced very low light output (undetectable by the eye).^{13,14} Elliott et al. recently reported luminance levels on the order of 25 cd/m² from similarly “precharged” Ru(bpy)₃²⁺-based polymer films.¹⁵

These solid-state precharging schemes failed to produce the high brightness and efficiency afforded by liquid ECL cells. We have shown that solid-state thin-film devices based on Ru(II) complexes can be activated to high brightness without any elaborate solvent- or temperature-assisted precharging processes. Luminance levels in the range of 50–200 cd/m² with external quantum efficiencies of 1% have been achieved with spin-cast films of Ru(bpy)₃²⁺-based polyurethanes.¹² High-efficiency devices operating in the 1–3% range were realized with a Ru(bpy)₃²⁺-based polyester that had been assembled into thin films by an aqueous layer-by-layer sequential adsorption process.^{17–19} All of our devices, however, required relatively high operating voltages (typically >6 V) to achieve respectable luminance levels (>50 cd/m²). Thus, the full potential of these Ru(II) complexes to operate at high brightness, high efficiency, and low voltages and with minimal delay time still had yet to be realized.

We now report simultaneous satisfaction of all four criteria. In this paper, we show that simple, single-layer, spin-cast films

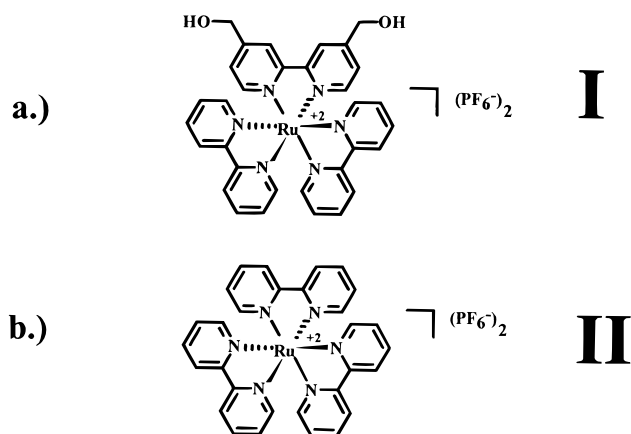
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- (20) Ma, Y.; Zhang, H.; Shen, J.; Che, C. *Synth. Met.* **1998**, *94*, 245. The devices described make use of osmium-bpy complexes.

Chart 1



of small-molecule Ru(bpy)₃²⁺-based complexes exhibit luminance levels as high as 1000 cd/m² at only 5 V and more than 200 cd/m² at 3 V. In addition, external quantum efficiencies as high as 1% can be realized at low voltages. Thus, solid-state devices with high brightness and efficiency have been achieved, for the first time, at near-redox potentials (2.5–3.0 V), affording devices with dramatically improved operating lifetimes. No elaborate film fabrication or “charging” schemes are required, and no reactive cathode materials (e.g., Ca, Mg) are needed. Red or red-orange luminance of this intensity is unparalleled in neat films of nonpolymeric emitters at these voltages. In addition, we suggest a simple means to minimize device response time using short, high-voltage pulses, followed by operation at lower voltages.

2. Experimental Section

The synthesis of Ru(bpy)₃²⁺ derivative **I** (Chart 1a) has been described earlier,¹⁷ and a more efficient synthesis has been outlined by Kocian et al.²¹ The latter procedure was followed in this work. The Cl⁻ salt of **I** was recrystallized from THF/H₂O; commercially available Ru(bpy)₃Cl₂ was used as received (Alfa Products). Counterion exchange to PF₆⁻ was accomplished via a metathesis reaction in which **I** and **II** (Chart 1b) were precipitated from aqueous solutions of the corresponding Cl⁻ salts and an excess of NH₄PF₆, washed with water, and dried. The esterified ligands employed in **III** and **IV** (Chart 2) were generated en route to the hydroxymethylated ligand of **I**.²¹ The overall syntheses of **III** and **IV** were similar to that of **I** and will be outlined in a future publication.

Using a photoresist spinner (Headway Research Inc., Garland, TX), thin films of **I–IV** were spin-cast onto 1-in. × 1-in. ITO (indium tin oxide)-patterned glass substrates from filtered 4% (w/w) pyridine solutions. The substrates had been sputtered with ITO (which served as the anode) by Donnelley Applied Films (Holland, MI) and patterned into 3-mm-wide strips by DCI, Inc. (Olathe, KS). Prior to spin-casting, the substrates underwent ultrasonic cleaning in 2:1 H₂O/Lysol solution for 10 min, followed by three 10-min ultrasonication steps in H₂O only. The ITO substrate used for **IV** was cleaned more rigorously by immersion in 1 M HCl for 1 min, followed by extensive rinsing with water. After the substrates were dried with compressed air, filtered pyridine was added to the substrates and spun off at 7000 rpm to rinse off any particulate. Solutions of **I**, **II**, and **III** were spun on at 1500 rpm for 30 s (yielding 700–1000-Å films), and **IV** was spun at 1000 rpm for 30 s (yielding a 1800-Å film). After spinning, all films were annealed under dynamic vacuum for several hours to remove residual pyridine. Specifically, samples were placed in a vacuum oven, the oven was evacuated, and the temperature of the oven was ramped up to 100 °C. (The oven requires roughly 1 h to reach 100 °C.) Two hours after the ramping was started, the oven was turned off, and the samples were

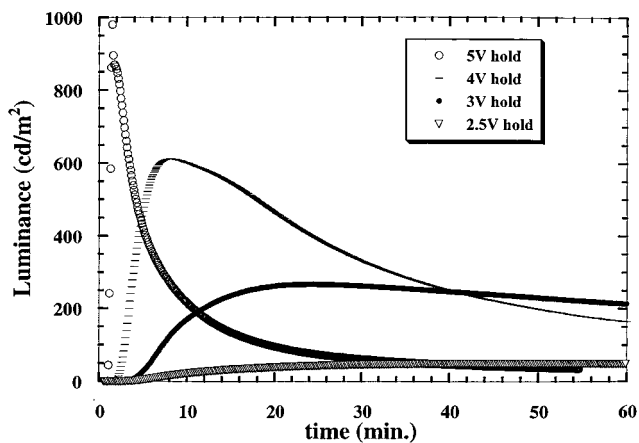
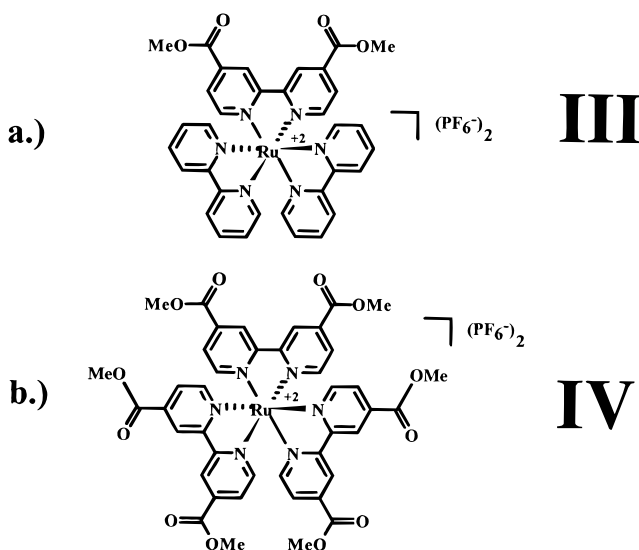


Figure 1. Light output as a function of time and applied voltage for solid-state devices based on **I**.

Chart 2



allowed to cool to room temperature under vacuum. An aluminum cathode was thermally evaporated on top of the film in 2-mm-wide, 1-in. strips to complete the device. In this way, a light-emitting active area (hereafter referred to as a “device”) of 6 mm² was defined. Device testing was computer-automated using the Labview (National Instruments, Austin, TX) program and performed in a glovebox in a nitrogen environment. Power was supplied by a Keithley 230 programmable voltage source. Unless otherwise indicated, devices were ramped to and held at the stated voltage. The voltage sweep rate used was 0.5 V/5 s. Current flow was measured using a Hewlett-Packard 34401A multimeter, and the emitted light intensity was measured using a Newport 1830C optical power meter. Calculation of external quantum efficiencies for these devices was described earlier.¹¹

3. Results and Discussion

One of our best performers to date is the hydroxymethylated Ru(bpy)₃²⁺ derivative **I** (Chart 1), originally developed for the synthesis of the polyurethanes¹² mentioned earlier. Figure 1 shows that devices fabricated from **I** reach luminance levels in the 600–1000 cd/m² range when biased at 4 or 5 V. At only 3 V, luminance levels in excess of 200 cd/m² are easily realized. This figure also shows that these high luminance levels are reached in a relatively short time at the highest voltages (about 2 min at 5 V), but only after about 20 min at the lower voltages. Device operation at such low voltages supports an electrochemical mode of operation and suggests a close parallel with liquid cell operation.¹ Tokel and Bard reported an oxidation potential

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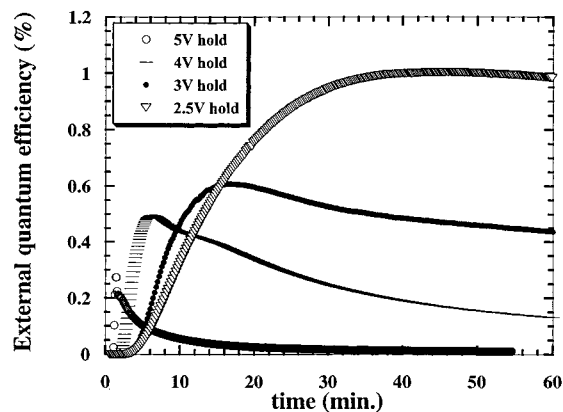


Figure 2. Device efficiency (% external) as a function of time and applied voltage for **I**.

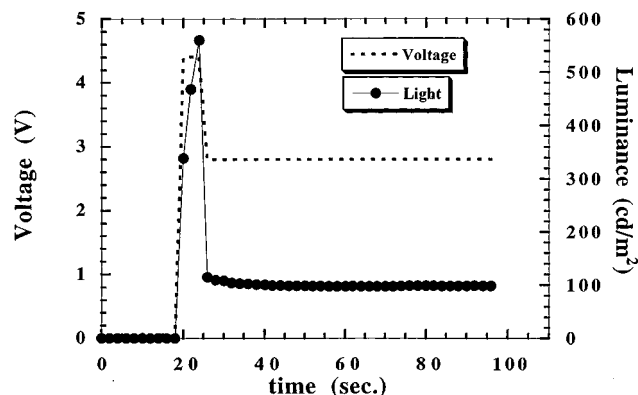


Figure 3. Light output as a function of time and applied voltage for a device based on **I**. An initial voltage pulse to 4.4 V was applied, followed by operation at 2.8 V. With this protocol, the device operates at low voltage and high brightness with minimal delay time.

of +1.63 V [Ru(III/II)] and a reduction potential of -1.09 V [Ru(II/I)] for Ru(bpy)₃Cl₂ (vs Ag wire reference) in aqueous solution.¹ This indicates a redox potential (difference in formal potentials for the two redox couples) of 2.72 V which is close to the lowest potential applied in this study (2.5 V, which produces ca. 50 cd/m²). In the solid state, the Ru(II) complex is oxidized to Ru(III) at the anode and reduced to Ru(I) at the cathode, as described earlier.^{11,13,14} Excited-state Ru(II)*, a product of the reaction between Ru(III) and Ru(I), decays radiatively to produce red-orange light ($\lambda_{\text{max}} = 630$ nm). The required PF₆⁻ counterion redistribution is slow at low bias, accounting for the sluggish device operation exhibited in Figure 1.

While the devices were more luminescent when operated at higher voltage, their external quantum efficiency and stability over time were better at low voltage. As shown in Figure 2, external efficiencies of 1% and roughly 0.3% were realized at 2.5 and 5 V, respectively. With regard to device stability, the emitted light intensity at 3 V dropped to one-half its maximum value 2 h after the potential was first applied (i.e., $t_{1/2} = 2$ h) but exceeded 10 cd/m² for 40 h of continuous operation. A $t_{1/2}$ of only 5 min was observed at 5 V.

Figure 3 demonstrates that devices based on **I** can be driven nearly instantaneously to respectable luminance levels. This was accomplished with a simple procedure involving a pulse to high voltage followed by operation at a lower voltage. In Figure 3, the bias was initially pulsed to 4.4 V for a few seconds and then lowered to 2.8 V. The net result was the nearly immediate realization of a luminance level of 100 cd/m². The device efficiency was roughly the same as that measured at the lower

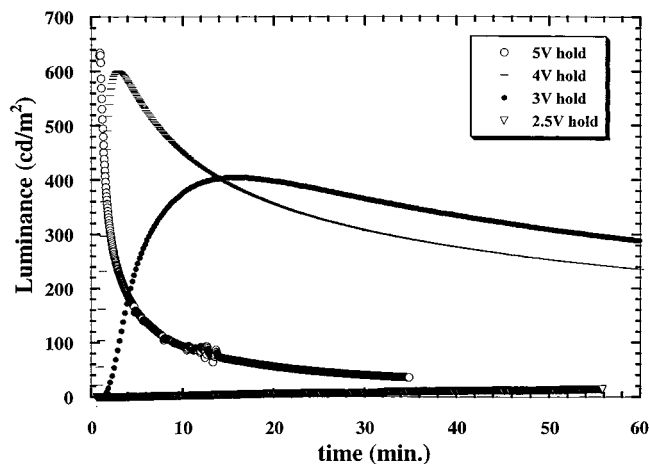


Figure 4. Light output as a function of time and applied voltage for devices based on **II**.

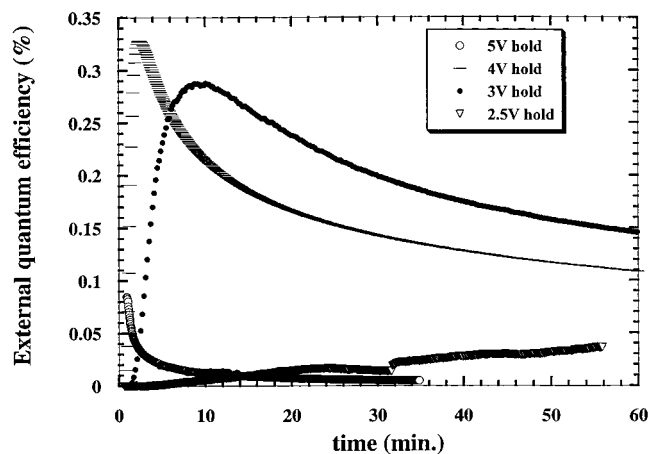


Figure 5. Device efficiency (% external) as a function of time and applied voltage for **II**.

voltage by the slower “charging” route. The use of such a voltage protocol overcomes, to a large extent, the sluggish device response ordinarily observed at lower voltages.

Devices based on **I** are not unique in their performance. The same basic device characteristics are exhibited by many small-molecule derivatives of Ru(bpy)₃²⁺, as well as by the unmodified version of this well-studied material, **II** (Chart 1). Light and efficiency versus time plots generated at different voltages for **II** are shown in Figures 4 and 5. While their luminance levels were comparable, devices based on **I** were generally more efficient than those based on **II**. At best, the latter operated at 0.3–0.4% efficiency (4 V), compared to 1% (2.5 V) in the former. Figure 5 shows that the 2.5-V efficiency of a device based on **II** reached only ~0.05% after 1 h. Like the devices based on **I**, however, those based on **II** could be induced to readily produce high luminance levels at low voltage with an initial high-voltage pulse. Preliminary work with **II** suggests that such a pulsing scheme affords devices that can be operated for up to 120 h with luminance levels in excess of 10 cd/m². In general, the long-term stability of **II** was somewhat better than that of **I**. After 40 h of continuous operation at 3 V, for example, the emission from **II** still exceeded 25 cd/m².

The structures of two other promising derivatives are shown in Chart 2. Lumophores **III** and **IV**, esterified versions of **II**, produce light of a more technologically useful red color ($\lambda_{\text{max}} = 690$ nm), rather than the red-orange emission (630 nm) of **I** and **II**. Other workers^{22,23} have measured a similar red shift in solution photoluminescence from the ethyl ester analogue of

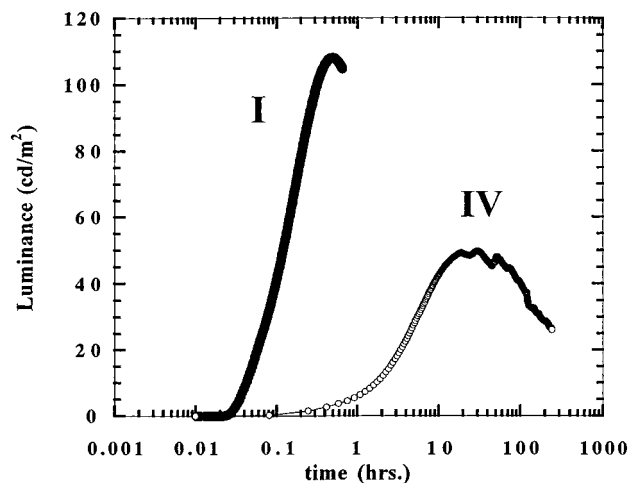


Figure 6. "Charging" profile of a device based on **I** (●) relative to **IV** (○).

IV, relative to that of $\text{Ru}(\text{bpy})_3^{2+}$. Luminance levels in the 50–600 cd/m^2 range and device efficiencies of 0.1–0.4% are typical for **III** and **IV** at 3–5 V. Film thicknesses for devices based on **III** and **IV** were roughly 700 and 1800 Å, respectively. For comparison, the devices based on **I** and **II** described earlier employed 800–1000-Å films. The 3-V charging times, however, are considerably longer for both **III** and **IV** (roughly 1.5 and 20 h, respectively) than for **I** and **II** (15–20 min). In addition, devices based on **III** and **IV** have significantly enhanced operating lifetimes relative to those based on **I** and **II**. At 3 V, $t_{1/2}$ values of roughly 30 (extrapolated) and 240 h were determined for **III** and **IV**, respectively. A longer charging time might be expected for **IV**, given that the spin-cast film of **IV** was roughly twice as thick as the films of **I** or **II**. Since the electric field at 3 V is smaller across the thicker film of **IV**, one might assume that counterion redistribution would be slower as a result, leading to the significantly longer charging time exhibited by **IV**. However, a device based on a film of **I** with a thickness comparable to that of **IV** (~1700 Å) still exhibited a 3-V charging time of 30 min, only 5–10 min longer than those for the thinner-film devices of **I** discussed earlier. The light vs time profile for a device based on this thicker 1700-Å film of **I**, relative to that of **IV**, is shown in Figure 6. Hence, film thickness is not the sole source of the longer charging time. The true mechanisms responsible for the more sluggish device response and improved operating stability in **III** and **IV** are currently under investigation. Solid-state photoluminescence measurements suggest that electrogenerated excited states may be more effectively quenched in thin films of **III** and **IV**, accounting for the lower device efficiencies. On the other hand, we have evidence to suggest that device efficiency is improved somewhat by acid-etching the ITO prior to spin-casting. As noted in the Experimental Section, the ITO substrate used for **IV** was immersed in 1 M HCl for 1 min, while substrates used for **I**, **II**, and **III** were not. As such, the observed device

efficiency of **IV** may actually be higher than what would be observed using unetched ITO. In any event, charging times do not appear to be affected by etching. More device testing and spectroscopic work are required to confirm and explain all of these observations.

4. Conclusion

In summary, high brightness, high efficiency, and good stability have been realized with thin-film solid-state devices based on $\text{Ru}(\text{bpy})_3^{2+}$ complexes at very low voltages. Device fabrication and operation are remarkably straightforward. Emitted light is red-orange in color for **I** and **II** and very intense. At 2.5 V, devices based on **I**, a hydroxymethylated derivative of $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$, operate with a luminous efficacy of 1.4 lm/W (0.6 cd/A), making **I** particularly attractive for flat-panel display application. Previous attempts to realize practical solid-state Ru(**II**)-based devices have employed films which were excessively thick or that possessed inadequate ionic conductivity. When thin films based on small molecules are employed, *an applied bias close to the redox potential of the emitter is sufficient to both induce counterion migration and effect the required redox reactions*. At slightly higher voltages, charging times decrease dramatically, but they do so at the expense of device efficiency and stability. If high voltage is applied only briefly, however, followed by normal operation at low voltage, the charging time requirement can be virtually eliminated. The exact high voltage required for this pulsing technique is a function of the degree to which the device had been previously conditioned. That is, this technique is more effective in devices that have been recently operated, and less so in "fresh" devices which have never been operated.

By replacing one or more ligands on $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ with another closely related, esterified bipyridine ligand (as in **III** and **IV**), the color of emission can be shifted from red-orange ($\lambda_{\text{max}} = 630 \text{ nm}$) to a more technologically useful red color (690 nm) with little change in luminance and with a concomitant 10–100-fold increase in device stability. Preliminary results suggest that other alternative biasing schemes (such as imposing an ac field over a dc bias across "precharged" films) also extend device lifetime severalfold at comparable brightness. Using thicker films of **I** spin-cast onto acid-etched ITO, we have recently achieved luminance levels in the range of 300–700 cd/m^2 and 1% efficiency at only 3–3.5 V. Without such processing modifications, devices which operate at 1% efficiency produce luminance levels of only 50 cd/m^2 (vide supra). These intriguing new results invite further exploration of better processing techniques, and continued improvement in these small-molecule devices is expected.

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