

Solid-State Organic Light-Emitting Diodes Based on Tris(2,2'-bipyridine)ruthenium(II) Complexes

Frank G. Gao and Allen J. Bard*

Department of Chemistry and Biochemistry
The University of Texas at Austin
Austin, Texas 78712

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In this contribution we report organic light-emitting diodes (OLEDs) fabricated on ITO (indium tin oxide, 100 Ω /square)-coated glass substrates with solid films of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ and its derivative $(\text{bpy})_2\text{Ru}(\text{II})[\text{bpy}(\text{COOC}_{12}\text{H}_{25})_2](\text{ClO}_4)_2$ [represented as $\text{C}_{12}\text{-Ru}(\text{bpy})_3(\text{ClO}_4)_2$] as light emitters (Figure 1). The ITO was the positive contact and a Ga:In eutectic (75.5:24.5 wt %, mp 15.7 $^\circ\text{C}$) or a vacuum-evaporated aluminum contact served as the electron injecting (negative) electrode. The current– and luminance–voltage plots show a diode-like behavior with a turn-on voltage of 2.3 V. A brightness of 500 cd/m^2 at 3 V bias and 2000 cd/m^2 at 4.5 V bias, quantum and power efficiencies of 1.4 and 0.8%, respectively, and a delay time (time required to reach maximum luminance) of 1 to 2 s under a constant 3 V bias were realized. An emission maximum at 660 nm was clearly visible as a bright red emission in a lighted room (Figure 2).

Electrogenerated chemiluminescence (ECL) of tris-chelated ruthenium(II) complexes in solution has been studied extensively.^{1–5} In dry acetonitrile, a quantum efficiency of 24% for ECL emission has been reported.¹ ECL has also been observed in polymer films of poly- $\text{Ru}(\text{vbpy})_3$ ^{6,7} and molten $\text{Ru}(\text{bpy})$ salts with the attachment of two ester-linked poly(ethylene glycol) tails,⁸ although their ECL efficiencies were low (0.035–0.1%). More recently, with the growing interest in solid-state OLEDs, efforts have been made to investigate OLEDs based on thin films of polymers or small molecules.⁹ These have included blends of tris-chelated ruthenium(II) complex and a conducting polymer¹⁰ as well as films of tris-chelated ruthenium(II) complex polymers.^{11,12} The external quantum efficiencies of these devices ranged from 0.06 to 1%, with turn-on voltages of 2.5 to 3 V, and rather low luminance levels (typically 25 to 200 cd/m^2 under a 6–10 V bias) and long turn-on times (taking about 0.5–2.5 min to reach maximum luminance under a 6 V constant bias). A recent report¹³ demonstrated an increase in emission brightness by employing salts of $\text{Ru}(\text{bpy})_3^{2+}$ and the hydroxymethylated and esterified derivatives as emitters. These exhibited luminance levels of 200 cd/m^2 at 3 V and 1000 cd/m^2 at 5 V (~1% quantum efficiency). However, the delay time to maximum emission with these was significant (10–15 min at 3 V and 1 min at 5 V).

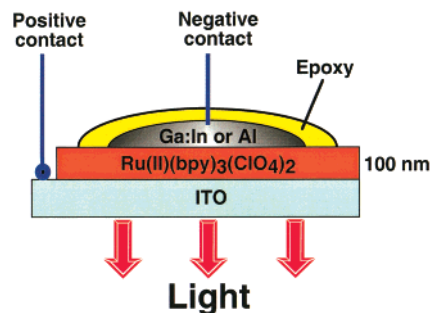


Figure 1. Structure of the OLED cell.

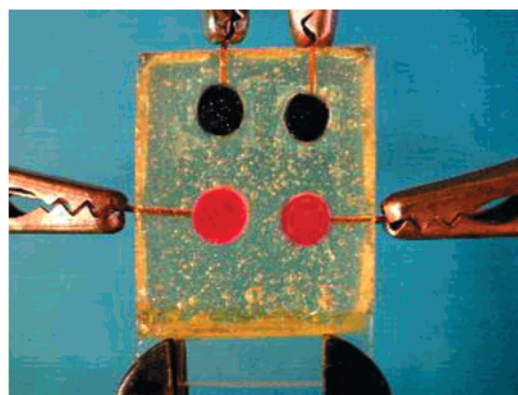
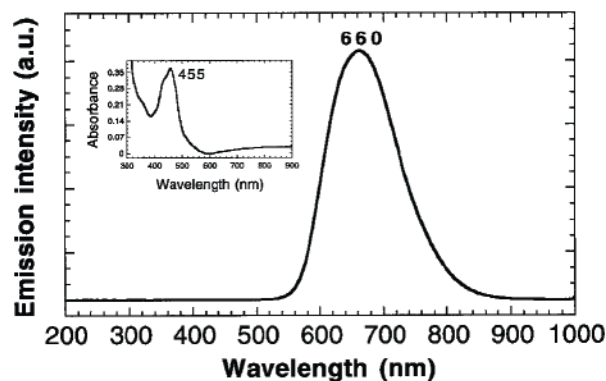


Figure 2. (Upper) Emission spectrum of a single layer OLED ITO/ $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2/\text{Ga:In}$, obtained under 3.1 V bias. Exposure time 500 ms. The CCD camera was cooled to $-114\text{ }^\circ\text{C}$. The inset is the optical absorption spectrum of the ITO/ $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ thin film. (Lower) Photograph showing emission from two contacts.

Commercially available $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was converted to $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ by a metathesis reaction with an excess of NaClO_4 .¹ The synthesis of the derivative of $\text{C}_{12}\text{-Ru}(\text{bpy})_3(\text{ClO}_4)_2$ followed the procedure reported previously.¹⁴ Thin films (about 100 nm thick) of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ were spin-coated onto $1.6 \times 2.2\text{ cm}^2$ ITO substrates from a 4% (w/v) acetonitrile solution at room temperature. Thin films (about 80 nm thick) of $\text{C}_{12}\text{-Ru}(\text{bpy})_3(\text{ClO}_4)_2$ were spin-coated onto ITO sheets from a 4% (w/v) pentanone solution. In some cells, N,N' -bis(3-methylphenyl)- N,N' -diphenyl benzidine (TPD) was used as a hole transport layer inserted between the ITO and the emitter layer. In these, a 0.7%

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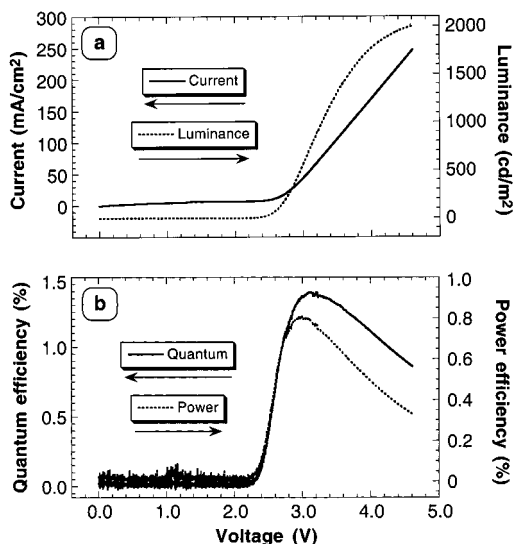


Figure 3. (a) Current–voltage and luminance–voltage plots of a single layer OLED, (+)ITO/Ru(bpy)₃(ClO₄)₂/Ga:In(–). The voltage scan rate was 0.05 V/s. (b) External quantum efficiency and power efficiency as a function of the voltage bias, obtained from the data in Figure 3a.

TPD (w/v) xylene solution was used to form a 20 nm thin film by spin-coating. All films were heated in a vacuum oven at 125 °C for 8 h. The Ga:In eutectic contact (about 3 mm diameter) was printed on top of the film and connected via a thin copper wire inserted into the Ga:In ball; both were then sealed with epoxy cement. Alternatively, an Al cathode was vacuum evaporated at a pressure of 2×10^{-6} Torr on the film.

The current–voltage and luminance–voltage plots of a single layer OLED (+)ITO/Ru(bpy)₃(ClO₄)₂/Ga:In(–) (forward voltage bias) showed a turn-on voltage of about 2.3 V for both current and emission (Figure 3a). The device reached a luminance level of 500 cd/m² at 3 V and a maximum luminance of 2000 cd/m² at about 4.5 V. Plots of external quantum efficiency and power efficiency as a function of the voltage bias (Figure 3b) show that with a voltage bias above 2.3 V the quantum efficiency and power efficiency rapidly increased with the voltage. At about 3.0 V, they reached maximum values of 1.4 and 0.8%, respectively, and then slowly decreased with a further increase in voltage. Results of a group of 20 OLEDs prepared by the same procedure showed considerable variations in external quantum efficiency ranging from 0.4 to 1.8%, and power efficiencies of 0.2 to 1.2%. Under reverse bias (ITO, negative; Ga:In, positive) a current flow is observed, but the emission is less than about 5 orders of magnitude than for comparable applied voltage in forward bias mode.

Figure 4 shows the current and luminance curves against time upon application of a 3.0 V voltage step. The time delay for the rise of the emission was only about 0.02 s; with about 1–2 s needed to reach the maximum luminance output. Variations in delay time were observed among the devices, ranging up to 1–5 s. The emission began to decrease soon after it reached the maximum. Typically there was a 50–60% drop of the initial luminance in 1 h. The intensity of the emitted light continued to decrease to a low level over several hours and then maintained a nearly steady level; after 5 h the emission was still visible with an intensity of about 20 cd/m². The higher the applied voltage,

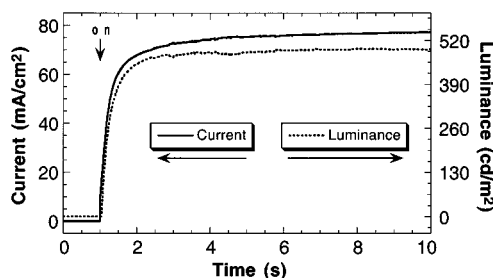


Figure 4. Current and luminance rise curves against time upon application of 3.0 V voltage bias, for the OLED: ITO/Ru(bpy)₃(ClO₄)₂/Ga:In.

the shorter was the delay time for the emission rise, but also the shorter was the time for emission to decay to one-half its initial value.

As shown by the emission spectrum in Figure 2, the luminescence from the single layer OLED was red with a peak wavelength at 660 nm and a half-maximum width of 140 nm. This is considerably red-shifted from the Ru(bpy)₃²⁺ emission found in solutions of acetonitrile or water (~610 nm). No, or only a very small (≤ 10 nm), blue-shift was observed when the bias increased from 3.1 to 9.4 V. The inset of Figure 2 shows the optical absorption spectrum of the ITO/Ru(bpy)₃(ClO₄)₂ thin film, indicating an absorption maximum wavelength at 455 nm.

For comparison, we also investigated the OLEDs with TPD as a hole transport layer inserted between the ITO and Ru(bpy)₃(ClO₄)₂ layer, (+)ITO/TPD/Ru(bpy)₃(ClO₄)₂/Ga:In(–). Results of a group of 20 bilayer OLEDs showed about the same performance as the cells without the TPD layer, except that there was a ~10 nm blue-shift in the emission maximum. Thus, a TPD layer did not significantly improve the performance of the OLED cells which appear to be largely governed by the quality of the Ru(bpy)₃(ClO₄)₂ thin films formed on ITO substrates (i.e., their smoothness, homogeneity, and freedom from pinholes).

The OLEDs employing only C₁₂–Ru(bpy)₃(ClO₄)₂ as an emitter were less efficient than Ru(bpy)₃(ClO₄)₂. However, OLEDs of the form ITO/Ru(bpy)₃(ClO₄)₂/C₁₂–Ru(bpy)₃(ClO₄)₂/Ga:In showed a performance closer to those of the single layer Ru(bpy)₃(ClO₄)₂ cells. The emission spectra of the OLEDs employing C₁₂–Ru(bpy)₃(ClO₄)₂ as emitter had a maximum wavelength at 690 nm and half-maximum width of 100 nm, with better color purity and a relatively narrower spectrum.

We are currently characterizing the devices to obtain a better understanding of the mechanism of operation and emission decay. Preliminary transmission electron microscope images of spin cast films of Ru(bpy)₃(ClO₄)₂ suggest the films are amorphous with any crystallites of size <5 nm. Emission probably occurs through electron injection into a bpy ligand at the negative electrode and hole injection into a Ru(II) center at the positive electrode. Electric field-driven electron and hole hopping occur until these are localized on a single molecule producing the excited state of Ru(bpy)₃^{2+*}.

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