

Highly efficient and bright electroluminescent Ru(bpy)₃(ClO₄)₂/Alq₃ device

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Electroluminescent devices of indium tin oxide (ITO)/Alq₃(212 nm)/Ru(bpy)₃(ClO₄)₂(100 nm)/Ga:In were fabricated and showed high external quantum and power efficiencies, of 6.4% and 5.3%, respectively, at an optical output power of 0.4 mW/cm² under a bias of 2.3 V. At a higher bias voltage (>2.7 V), the output power was well above 10 mW/cm², but with a lower efficiency. Light emission occurred at the interface between Alq₃ and Ru(bpy)₃(ClO₄)₂, whose relative energies of both excited and ground states were offset, ideal for confining both charge carriers and minimizing the quenching of the Ru(bpy)₃²⁺ excited state. By comparison, in a single layer device without Alq₃, the emission zone was located at the ITO interface where excited states were quenched and electron injection from the reduced molecules to the ITO contact produced a unipolar current and thus lower efficiency. © 2005 American Institute of Physics. [DOI: 10.1063/1.2009079]

The performance of organic light-emitting devices (LEDs) has improved considerably since initial studies on small molecules¹ and conjugated polymer² devices, and the external quantum efficiency (η_{ext}) now reaches a few percent. Doping with dye molecules also enhances the efficiency.³ Recently, Ru(bpy)₃(ClO₄)₂-based single layer solid-state light-emitting electrochemical cells (LECs) have shown interesting properties^{4–12} and individually addressable submicron scale LEDs have been fabricated.⁸ Here we show that in the single layer, LECs emission occurs at the interface between the Ru(bpy)₃(ClO₄)₂ and indium tin oxide (ITO) anode, with a large loss in efficiency from the unipolar flow of electrons into the anode. This undesired process could be minimized, however, by inserting a layer of aluminum 8-hydroxyquinoline (Alq₃) at the anode interface to shift the location of the emission to a new interface between Alq₃ and Ru(bpy)₃(ClO₄)₂. Under these conditions, the efficiency was significantly improved without a decrease of optical output power and increase in turn-on voltage. For example, when a bias voltage of 2.3 V was applied to the two layer LEC, an η_{ext} of about 6% was obtained at an output power of 0.4 mW/cm². The emitted red light peaked at 630 nm, a signature for emission of Ru(bpy)₃(ClO₄)₂ rather than for Alq₃ that emits in the green regions at around 530 nm.

To determine the location of the emission in the Ru(bpy)₃(ClO₄)₂ based single layer LEC, an open-face configuration was used.¹³ The ITO electrodes were lithographically fabricated into five parallel and separate fingers,⁸ on which Ru(bpy)₃(ClO₄)₂ was spin coated to form an open-face LEC, with the two neighboring 5 μm wide ITO fingers spaced 5 μm apart serving as anode and cathode. The spin coating of the Ru(bpy)₃(ClO₄)₂ was performed from an acetonitrile solution followed by heating in a vacuum oven at 150° for about 72 h to produce films about 500 nm thick. Samples were placed on an inverted optical microscope (Model TE 300, Nikon) and images of the emission could be taken with a camera (Model 7404-0001, Roper Scientific, Inc.) during operation. With an applied voltage of 40 to 45 V, the emission was seen at the edge of the anode ITO finger. With this large (5 μm) electrode spacing, emission was not

detectable at a bias below 35 V (as opposed to the ~2.5 to 3 V bias used for 100 nm thick cells). Interestingly, for samples that were not heated after spin coating, the results were very different. For these, under a bias of 8 V, transient current and light were detected and the rise and fall to negligible current levels occurred in only a few minutes and light emission was seen at the cathode. All of the data shown in this letter were obtained from heated (dry) samples only. Under continuous operation, the intensity of emitted light at some locations diminished over time, however, there were areas where emitted light was clearly seen for an experimental duration of about 2 h. When the sign of the bias voltage was changed so that the previous cathode became an anode (and vice versa), the position of emission shifted to the edge of the new anode. Repeated switching of the anode and cathode confirmed that the emitting centers were always located at the edge of the anode independent of which ITO finger was used. Moreover, the emission turned on quickly and was clearly seen in the very first image (with an integration time for the charge coupled device camera of 2 s) with no delay noticed during the switching between anode and cathode. The same conclusion was reached with 1 μm wide ITO fingers separated by a 1 μm gap under a bias voltage of 8 V.

Interestingly, when the bias was increased to 10 V, emission was seen from whole surface of the ITO anode as shown in Fig. 1. In this image, the emission zone appeared a little wider than it actually is due to image blooming. Emission in this case probably came only from “hot” spots at the ITO edge under low bias voltage, while the whole area was turned on at higher bias. Note that the electric fields in these ITO finger-based open-face LECs were several times weaker than those in the single layer sandwich Ru(bpy)₃(ClO₄)₂ ones.^{4–6,8–10} Moreover, the cathode material, e.g., Ga:In, used in sandwich LECs has a lower work function compared to the ITO cathode used here. The emission probably also is localized at the interface between the ITO anode and the Ru(bpy)₃(ClO₄)₂ film in dry single layer LECs. In fact, recent studies of these LECs clearly indicated that electrons were injected early at low bias producing a unipolar current, while holes were injected later at high bias during a voltage scan.^{10,11} This means that electrons were already near the ITO anode before holes are injected to start the emission,

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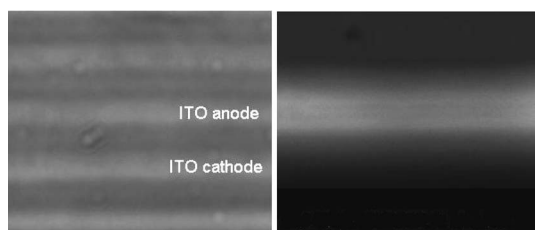


FIG. 1. *Left*: Image of lithographically fabricated individually addressable one micron wide ITO electrodes separated from each other by a one micron gap. The surface was spin coated with a $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ film. *Right*: Image of electroluminescence at the same location when a bias voltage of 10 V was applied to the two ITO electrodes as indicated in the top image.

consistent with the observations shown in Fig. 1.

In general, relative injection rate and charge carrier mobility are the two independent factors governing the location of the emission zone. If the mobilities of electrons and holes are identical and the two charge carriers are injected at the same time in a single layer LED, the emission would first occur at the middle of the film. However, when one electrode, the cathode for example, injects charge first, and the cell thickness is small, a unipolar current can result, and the emission zone will be nearer the anode surface. In general, when the fluxes of electron and hole are different, the emission zone will approach one of the electrodes at steady state depending on which flux is larger independent of where the two charge carriers meet initially. However, shifting of the emission zone from anode toward cathode was not seen in the $5 \mu\text{m}$ ITO finger electrode open-face cell over a period of 2 h under continuous operation. This result suggests a potential problem with the single layer LECs, since the excited state near the anode surface can be quenched by the ITO electrode. In fact, about a 15% reduction in photoluminescence intensity was observed when a $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ film was deposited on an ITO surface compared to a similar film on a bare glass substrate. Moreover, such a process was observed in a photoelectrochemical thin-film sandwich cell, where a photocurrent under short-circuit conditions with optical excitation was clearly seen.⁸ In this cell with photoexcitation, the photocurrent increased dramatically with increasing bias voltage with the illuminated ITO positive.⁸ In fact, many organic molecules can inject electrons from their excited states into the ITO electrode to generate an anodic current under short-circuit conditions in symmetrical sandwich cells, i.e., ITO/organic molecule/ITO, where no external drive force exists, and the current always increases greatly under a positive bias.¹³ The electron transfer quenching of the excited state in such photoelectrochemical cells is clearly related to a similar quenching phenomenon in the LECs. This quenching effect occurs along with the loss in current efficiency (fraction of the current that produces excited states) by the unipolar electron current, which injects charge directly into the ITO anode.¹⁰ Obviously, the existence of this current will also significantly reduce the emission efficiency.

When a layer of Alq_3 (212 nm thick) was introduced on the ITO to separate the anode from the $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ layer, the current density was significantly reduced and the emission efficiency dramatically increased, since the unipolar current was effectively blocked. As shown in Fig. 2, the energy barrier between the two molecules helped to confine the charge carriers to the new interface as compared to the

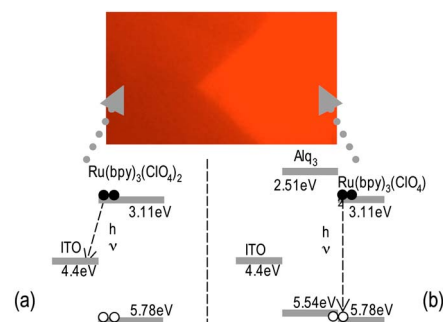


FIG. 2. (Color online) *Top*: image of electroluminescence from an area with both single (left) and dual layer (right). The addition of Alq_3 made the luminescence brighter, although the current density in single layer was actually higher. *Bottom*: relative energy levels near the anode of (a) single layer and (b) dual layer LECs. The shift of emission zone from the interface in single layer to the bulk in the double layer LECs effectively blocked the electron injection from the excited states into the ITO anode and thus increased the emission efficiency. These diagrams were constructed based on electrochemical measurements of the redox potentials corrected to solid-state energy levels of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ and Alq_3 , and the work function of heavily doped ITO.

original one leading to a brighter luminescence (Fig. 2, top). Note that the construction of the energy level diagram shown in Fig. 2 was based on electrochemical measurements of redox potentials of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$,^{10,14} since the more frequently used ultraviolet photoemission spectroscopic data for this molecule was not available. Although the energy levels for Alq_3 are shifted negative compared to UPS data, this should not make a significant difference for relative comparison between these two molecules.

Since Alq_3 has also been used as an emitter in previous LEDs,¹ it was important to determine if one or both molecules were responsible for the observed emission. The spectrum of the emission from the dual layer LECs shows a single peak at 630 nm; no peak was seen, even at higher sensitivity, in the region between 450 nm and 600 nm where Alq_3 normally emits. This indicates that the emission came only from $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ thus the emission zone was not near the ITO anode surface. In fact, an image of luminescence shown in the top of Fig. 2 clearly indicates that the addition of Alq_3 only enhanced the brightness without a color change. The samples were prepared by a vacuum deposition of 212 nm thick Alq_3 (Aldrich, 99.995%) on an ITO substrate followed by spin coating the $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ film⁵ and Ga:In alloy was used as the cathode.

To test the possibility that intermixing of the Alq_3 and the $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ occurred during the spin coating, the following experiments were carried out. First, following vacuum deposition, the Alq_3 film was washed with the same amount of pure acetonitrile as was in the spin coating, there was no apparent change, by eye or an optical microscope, after this treatment. The solubility of Alq_3 in acetonitrile is in fact small (0.2 mg/mL). In addition, current-voltage curves did not change significantly for a single layer Alq_3 device with and without treatment of the acetonitrile solvent indicating that possible subtle changes in the Alq_3 morphology did not appreciably affect the overall electrical properties. In another experiment, when excess Alq_3 was added to the regular spin-coating solution of acetonitrile containing $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$, the resulting single layer cell of ITO/ Alq_3 and $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ mixture/Ga:In showed a lower quantum efficiency compared to similar cells without Alq_3 . This

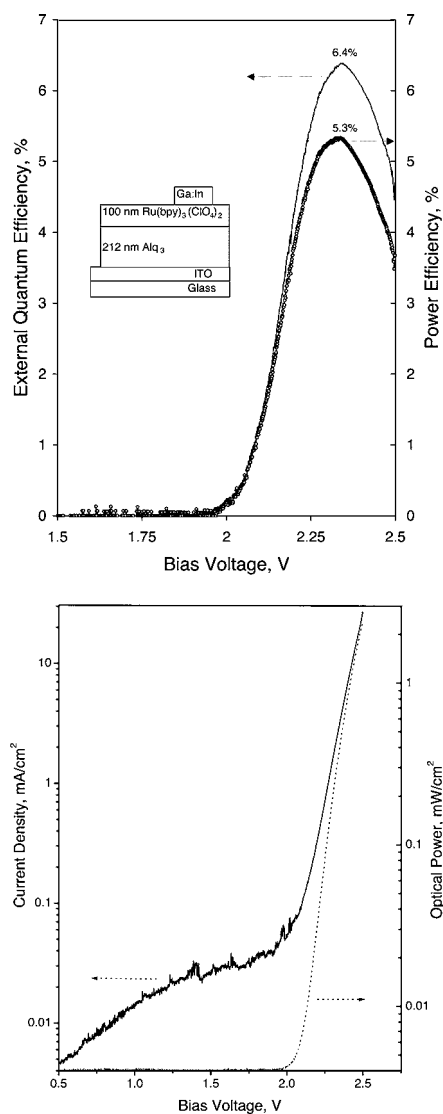


FIG. 3. *Top:* External quantum and power efficiencies as a function of bias voltage for a double layer LED of ITO/Alq₃/Ru(bpy)₃(ClO₄)₂/Ga:In as shown in the inset. *Bottom:* Current and optical output power vs bias voltage for the same LED with the ITO electrode as the anode.

means that a possible mixed structure of Alq₃ and Ru(bpy)₃(ClO₄)₂ was not responsible for the improvement observed with the double layer cell discussed above, although the interface between the two layers may indeed be slightly modified during the spin-coating process and thus may not be very sharp. A similar improvement was seen when a thinner Alq₃ layer (187 nm) was used for the two-layer device. Since an efficiency of about 6% is near the upper limit for a Ru(bpy)₃(ClO₄)₂ based device, the thickness of the Alq₃ was not systematically investigated for possible optimization. Light emission from single layer cell of ITO/Alq₃(212 nm thick)/Ga:In under a bias of about 3 V was also clearly observed as reported earlier.¹⁵ This demonstrated hole injection at the ITO/Alq₃ interface at low bias, although the efficiency was lower than that from

ITO/Ru(bpy)₃(ClO₄)₂/Ga:In. In the two layer cells, however, emission from Alq₃ was not seen. All measurements were carried out at room temperature under ambient conditions. Autolab and Newport Optical Power Meter (1830-C) were used in the measurements.

The dependence of current and the emission intensity as a function of bias voltage from the dual layer LEC, i.e., ITO/Alq₃/Ru(bpy)₃(ClO₄)₂/Ga:In, is shown in Fig. 3 (bottom), where the turn-on voltage for both current and emission was about 2 V. The lack of increase of turn-on voltage by the addition of the Alq₃ layer suggests that the emission process is controlled by the rate of charge injection at the electrodes rather than by resistance of the solid layers, as observed for either Alq₃ (Ref. 16) or Ru(bpy)₃(ClO₄)₂ (Ref. 10) based single layer LEDs. Ion movement-induced interfacial double layer formation probably played an important role in the charge injection.¹⁰ Figure 3 (top) shows the relation between bias voltage and η_{ext} and power efficiency, which reached about 6.4% and 5.3%, respectively, obtained under a bias of 2.3 V at an optical output power of 0.4 mW/cm², assuming an emission with a Lambertian distribution. The η_{ext} maximum generally varied from 6.1 to 6.8% for most measurements and reached as high as 7.5% in one case. At higher bias voltages (>2.7 V), the optical output power was well above 10 mW/cm². Note that this quantum efficiency is near the maximum level expected, given the photoluminescence efficiency of the Ru(bpy)₃(ClO₄)₂.

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