Individually Addressable Submicron Scale Light-Emitting Devices Based on Electroluminescence of Solid Ru(bpy)$_3$(ClO$_4$)$_2$ Films

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Received January 16, 2002

Very small light sources could find a number of applications in photonic devices, high-resolution sensors, and printers. Micrometer- and nanometer-size polymeric light-emitting devices were reported recently.[1,2] These patterned and randomly distributed LEDs, however, were not individually addressable, which is a crucial requirement for practical devices. Here, we report an individually addressable submicron scale LED based on a solid layer of Ru(bpy)$_3$(ClO$_4$)$_2$ (~100 nm thick). The emitted light with a bias voltage of 3 V peaked at a wavelength of 660 nm and was clearly visible under ambient room light with an optical microscope. This is probably the smallest individually addressable LED reported to date.

Solid film Ru(bpy)$_3$(ClO$_4$)$_2$ devices have been described previously and show a low turn-on voltage and high brightness.[3,4] In these devices, Ru(bpy)$_3$(ClO$_4$)$_2$ spin-coated from a MeCN solution on an indium−tin oxide (ITO) glass substrate and then dried at 145 °C in an Ar atmosphere for over 20 h produced amorphous films. These are provided with a top contact of Ga:In alloy to form a structure designated as ITO/Ru(bpy)$_3$(ClO$_4$)$_2$(a)/Ga:In.[3] However, in the present study the ITO electrodes were lithographically fabricated into five parallel and separate fingers with widths down to 0.9 μm and lengths of several mm. A Ga:In tip controlled by a micrometer was employed as a liftable electrode. Since the Ga:In alloy does not wet the film surface well, it was quite easy to make contact within a radius of a few tens of a micrometer and the tip could be relocated at different areas facing the ITO fingers of the same or different size. Light emission was seen from the ITO lines as shown in Figure 1. These two images were taken with an optical microscope with the sample biased at 3 V (ITO positive). Interestingly, defects on the ITO electrode resulting from the wet etching step in the array fabrication were clearly visible and the light from the edges appeared slightly brighter. The active layer was about 0.1 μm thick. The thinner ITO fingers shown here are about 0.9 μm wide and are separated from each other by 1.1 μm. This image also shows wider ITO fingers that were used to connect the LED to the external circuit.

Note that in addition to the unprecedented spatial resolution, Figure 1 also demonstrates the excellent brightness of the emission. By comparison, the emission from a polymer-based submicron LED was not visible at all under an optical microscope. In fact, an exposure time of 15 min was required for a camera to "see" the emission.[2] In our case, however, the emission was clearly seen by eye under ambient room light. Only LEDs such as this one with a high brightness can be made to achieve very high resolution.

Light emission from ITO/Ru(bpy)$_3$(ClO$_4$)$_2$(a)/Ga:In was detectable only when the ITO electrode was biased positive.[3] However, a current was also observed when a negative bias voltage was applied to the ITO electrode. When a carbon paste electrode, which was made from a mixture of carbon powder with mineral oil,[5] was used to replace the contact electrode of Ga:In, both current and
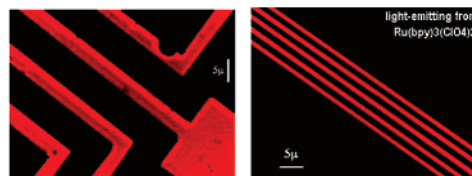
Figure 1. Light-emitting images from two different locations on an LED consisting of a lithographically fabricated ITO finger electrode, Ru(bpy)$_3$-(ClO$_4$)$_2$(a) active layer, and a Ga:In counter electrode. Bias voltage was 3 V with ITO positive. The emitted light was clearly seen by eye through an optical microscope. No light was emitted from those areas (appearing dark) where ITO was absent.

light were seen in each direction of the potential scan. This indicates that ITO is capable of injecting both charge carriers into the active layer and the lack of emission with a positively biased Ga:In contact in the ITO/Ru(bpy)$_3$(ClO$_4$)$_2$/Ga:In cell probably results from oxidation of this material rather than hole injection. Interestingly, with these carbon paste contact cells, stronger light emission was observed when the ITO was biased negative. Thus, the ITO electrode is probably a relatively better hole injector, as will be discussed below, and the two injected charge carriers are more imbalanced at the positive ITO bias leading to a lower emission efficiency. Despite the absorption effect from the dark carbon paste, an external quantum efficiency (total photons detected/electrons injected)[3] of about 0.15% was obtained at the peak of the light-emitting curve at about −3.45 V. Moreover, the turn-on voltage was very close to that obtained with the Ga:In electrode. The shelf life of the Ru(bpy)$_3$(ClO$_4$)$_2$-based devices was quite long and a 6-month-old film stored in air still worked well with either Ga:In or carbon paste cathodes.

To determine experimentally if the ITO electrode injected the two charge carriers equally or one preferentially over another, symmetrical LEDs were fabricated still using a single active layer sandwiched between two ITO electrodes, i.e., ITO/Ru(bpy)$_3$(ClO$_4$)$_2$-(xyl)/ITO, similar to a structure described earlier for zinc porphyrin devices.[6] In these latter devices, two ITO electrodes spaced about 1 μm apart form the cell and the material was capillary filled into the cell upon melting. Since Ru(bpy)$_3$(ClO$_4$)$_2$ cannot be melted to fill the cell, this procedure[6] could not be used. Thus, a nearly saturated acetonitrile solution of Ru(bpy)$_3$(ClO$_4$)$_2$ was injected into the empty ITO cell; crystals were produced after the solvent was evaporated at 105 °C in an oven. Repeated fillings eventually led to the formation of submillimeter-size single-crystal thin films (~1.5 μm thick) of Ru(bpy)$_3$(ClO$_4$)$_2$ within the two ITO electrodes. These were then heated in an Ar atmosphere at 180 °C for 21 h. The resulting film between two crossed polarizers as observed with an optical microscope is shown in Figure 2. Note that *only* a single crystal thin film will show colors between two crossed polarizers and the dark areas shown in the images are simply the open space in the cell. As expected, the single crystals in these thin films show sharp corners, e.g., 90° and 140° as shown in Figure 2.

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Figure 2. Images (0.15 mm × 0.12 mm) of Ru(bpy)$_3$(ClO$_4$)$_2$ single-crystal thin films (about 1.5 μm thick) between two crossed polarizers with an optical microscope. Dark areas are open air spaces. The two corners on the single crystal are 90° and 140°.
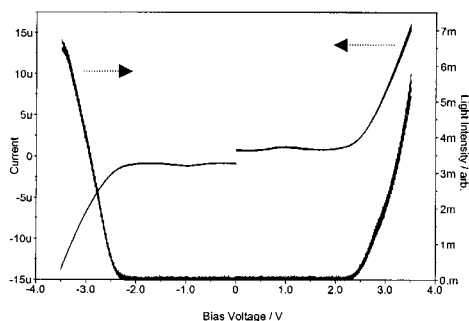
Figure 3. Current and light intensity as a function of bias voltage from a single-crystal LED of ITO/Ru(bpy)$_3$(ClO$_4$)$_2$(xyl)/ITO. Scan rate: 50 mV/s. Curves overlapped for over 30 consecutive scans in both directions.

Light was emitted from the ITO/Ru(bpy)$_3$(ClO$_4$)$_2$(xyl)/ITO cell under both positive and negative bias (Figure 3). A striking characteristic in this figure is that the curves of current and light intensity as a function of bias voltage were essentially identical for over 30 sequential scans in both directions. No hysteresis was observed. Another interesting phenomenon in this figure is that the turn-on voltage was essentially the same as that with the spin-coated amorphous film (100 nm) LEDs (about 15 times thinner than the single crystal ones). This suggests that the conductivity is significantly higher in the single crystalline thin film, so the *iR* drop is negligible. Note also that light intensity shown on the left consistently appeared a bit stronger. Since this LED was a symmetrical structure, the only explanation is that electrons and holes have different mobilities, so that the emitting zone where electron−hole recombination occurs was not in the middle of the active layer. The stronger light resulted from the emitting zone being closer by approximately 250 nm to the power meter so that the film absorbance (the crystalline film shows an appreciable absorbance at 660 nm at room temperature) and scattering have a relatively smaller effect. Since the higher light intensity was measured when the ITO contact facing the meter was negative, this indicates a higher hole mobility estimated to be about 1.4 times larger than that for the electron. The same result was obtained when the symmetrical sandwich cell was turned around, indicating that the observed effect was not due to differences in the nature of the ITO contacts.

An external quantum efficiency of 3.4%, significantly higher than these reported before[3,4] for light emission from the symmetrical sandwich cell was obtained. Note that no special care was taken to avoid the oxygen and moisture from the initial cell preparation to the end measurement. Preliminary stability tests under a fixed bias voltage of 3.5 V for continuous operation showed that the emitted light intensity was stable over 74 h without decay compared to a lifetime of only a few hours reported for amorphous film cells.[3,4] ITO/Ru(bpy)$_3$Cl$_2$(xyl)/ITO was also fabricated for comparison. Since Ru(bpy)$_3$Cl$_2$ is highly soluble in water, a saturated aqueous solution was used for the filling. Again, single-crystal thin films
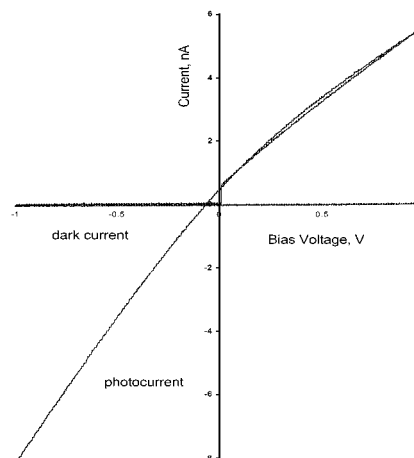
Figure 4. Photocurrent and dark current as a function of bias voltage from a single-crystal cell of ITO/Ru(bpy)$_3$(ClO$_4$)$_2$(xyl)/ITO. Scan rate: 50 mV/s. A 300 W projector light was used for irradiation.

were obtained and symmetrical I vs. V curves, which overlapped each other on repeated scans similar to Figure 3, were observed. The intensity of emission of this cell was about the same as that with the perchlorate salt.

This cell also behaved as a photovoltaic cell with charge injection at the ITO interfaces upon shining light on the ITO/Ru(bpy)$_3$(ClO$_4$)$_2$(xyl)/ITO cell under short-circuit conditions (i.e., without a bias voltage) (Figure 4).

Following the photogeneration of excited states to produce an equal number of electrons and holes near the illuminated interface, a short-circuit photocurrent (I_{sc}) was collected to determine which direction the two charge carriers move with no external electric field. We found that electrons were injected from the film into the illuminated ITO electrode (i.e., a steady-state anodic I_{sc} was observed). This indicated that it was more favorable for electrons from an excited Ru(bpy)$_3$$^{2+}$ molecule to be injected into the conduction band of the ITO electrode, while holes moved through the layer of Ru(bpy)$_3$(ClO$_4$)$_2$ to reach the dark counter electrode, just like earlier symmetrical porphyrin-based cells.[7] Note that the same result (the irradiated face was negative) was obtained when the light irradiated the opposite ITO electrode, just as with other symmetrical cells.[7] When a positive (or negative) bias voltage was applied to the illuminated ITO electrode, a steady-state anodic (or cathodic) photocurrent was seen. This means that the direction of the charge carrier movement could be reversed by an appropriate applied bias.

Overall, key factors including resolution, efficiency, stability, brightness, and turn-on voltage as well as the reversible photon and electron interconversion suggest that Ru(bpy)$_3$(ClO$_4$)$_2$(xyl) is a very promising material for LEDs and optoelectronic devices.

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JA0256156