

An organic red-emitting diode with a water-soluble DNA–polyaniline complex containing $\text{Ru}(\text{bpy})_3^{2+}$

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Received 29th March 2001, Accepted 27th April 2001

First published as an Advance Article on the web 16th May 2001

A $\text{Ru}(\text{bpy})_3^{2+}$ -based red-emitting diode with a fast turn-on response was fabricated by employing a novel, processable and water-soluble DNA–photopolymerized PAN complex containing $\text{Ru}(\text{bpy})_3^{2+}$.

Organic light emitting diodes (OLEDs) have been attracting keen interest in display technology, and some have already been on the market.¹ Several materials including organic molecules with low molar mass, metal-complexes and polymers have been proposed as hole-transporting, electron-transporting, and light-emitting materials.² OLED cells are commonly fabricated by vacuum evaporation for low molar mass materials, or by spin-coating and dipping for polymeric materials. Particularly, during the vacuum evaporation process, organic materials were evaporated by heating *in vacuo*. This heat treatment may result in a deformation of molecular structure and a reaction between molecules. These, therefore, limited a variety of applicable organic molecules. Even in the spin-coating process from organic solution, some solvents have the possibility of causing environmental problems. A simpler fabrication process from aqueous solution is required for mass production. On this basis, OLEDs with a water-soluble Ru complex as an emitter were fabricated using a simple preparation method.^{3–6} In particular, Rubner *et al.* reported that OLEDs fabricated with simple spin-casting of the solution of the Ru complex showed orange–red emission with a maximum luminance level of about 50 cd m^{-2} at current densities of about 1000 mA cm^{-2} .³ These OLEDs showed slow turn-on response with the time to achieve 90% of maximum luminance at a given voltage typically taking 10–120 second. The light emitting mechanism was believed to be electrochemical in origin. Direct hole and electron-injection from electrodes are required to achieve a fast turn-on response in such Ru complex-based OLEDs.

The Ru complex is also known as a photocatalyst; we have already reported the photopolymerization of aniline derivatives by the photocatalytic reaction of $\text{Ru}(\text{bpy})_3^{2+}$.^{7,8} A complex of photopolymerized polyaniline (PAN) with micelle,⁹ clay mineral,¹⁰ polyanion or DNA¹¹ can be easily prepared by photopolymerization in the presence of such an anionic template. In particular, more extended conjugation length of the photopolymerized PAN was obtained in the complex with DNA than others even under mild preparation conditions. Such a PAN complex included $\text{Ru}(\text{bpy})_3^{2+}$ in its matrix even after purification, because $\text{Ru}(\text{bpy})_3^{2+}$ could be electrostatically bound on the free anionic sites of the template, remaining after complexation with the PAN. $\text{Ru}(\text{bpy})_3^{2+}$ works as a

light-emitting molecule as well as a photosensitizer. PAN in the complex should be a *p*-type conductor. If DNA showed electronic conduction, as extensively discussed previously,^{12–15} and worked as an *n*-type conductor, the PAN–DNA complex containing $\text{Ru}(\text{bpy})_3^{2+}$ would be expected to be a photovoltaic molecular system, and a light-emitting molecular system where electrons and holes were injected from electrodes through DNA and PAN, respectively, and combined at $\text{Ru}(\text{bpy})_3^{2+}$ on the complex to emit red light. In this communication, we present the behavior of the red-emitting diode which is fabricated from a novel, processable and water-soluble DNA–photopolymerized PAN complex containing $\text{Ru}(\text{bpy})_3^{2+}$.

$\text{Ru}(\text{bpy})_3^{2+}$ was prepared according to the literature procedure and was then purified by recrystallization from water. Sodium salts of DNA from salmon testes were provided by the Nippon Chemical Feed Co., Ltd. The DNA–PAN complex was prepared by template photopolymerization of aniline derivatives as described previously,¹¹ and was purified by reprecipitation with acetone twice to remove unreacted aniline derivatives. The molar mass of the photopolymerized PAN in the DNA complex is not easily analyzed. However, the molar mass of the photopolymerized PAN without the template was estimated to be several thousand by GPC measurement.¹⁶ We believe the molar mass of the PAN photopolymerized in the presence of DNA is comparable or higher than several thousand by taking those UV-vis spectra into account. Since $\text{Ru}(\text{bpy})_3^{2+}$ should work as an emitter and the concentration of $\text{Ru}(\text{bpy})_3^{2+}$ in the DNA–PAN complex was not enough to fabricate an OLED, a solution containing $4.2 \times 10^{-3} \text{ g ml}^{-1}$ of DNA–PAN complex and $3.2 \times 10^{-4} \text{ g ml}^{-1}$ $\text{Ru}(\text{bpy})_3^{2+}$ was prepared by adding an appropriate amount of $\text{Ru}(\text{bpy})_3^{2+}$ to the solution. An indium–tin oxide (ITO)-coated glass electrode was dipped in the solution to prepare DNA–PAN containing $\text{Ru}(\text{bpy})_3^{2+}$ on the electrode. The film was dried at 80°C for 5 min. The thickness of the film was measured with Veeco/Sloan Technology Dektak³ Surface Profilers and was estimated to be 30–50 nm. The precipitate and crystal corresponding to $\text{Ru}(\text{bpy})_3^{2+}$ itself were not found in the micrograph of the film, indicating that the $\text{Ru}(\text{bpy})_3^{2+}$ incorporated was homogeneously dispersed in the film possibly due to electrostatic interaction between the phosphate groups of DNA and $\text{Ru}(\text{bpy})_3^{2+}$. The Al top electrode was finally deposited with a thickness of 100 nm at 4.0×10^{-6} Torr. The emitting area was $0.2 \times 0.2 \text{ cm}^2$. Luminance was measured with a Topcon BM-7 luminance colorimeter at room temperature, and emission spectra were measured with an Otsuka Electronics Photal IMUC 7000 system.

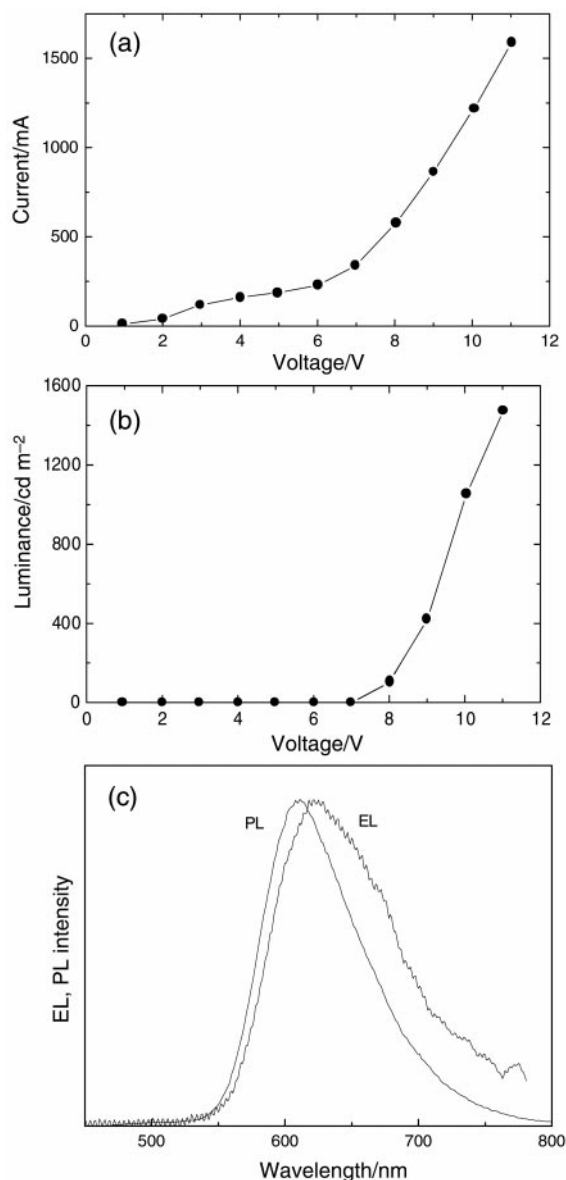


Fig. 1 Current–voltage characteristics (a) and luminance–voltage characteristics (b) of a DNA–PAN complex containing $\text{Ru}(\text{bpy})_3^{2+}$ device. PL spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ in an aqueous solution and device EL spectrum (c).

The current (I)–voltage (V) curve of the device is plotted in Fig. 1(a). The current abruptly increases above the bias voltage of 7 V, and a large current of 1600 mA is obtained at 11 V. This indicates that the current over 7 V obeys the space charge limited current (SCLC) mechanism. The current at 11 V is relatively higher than that of the device commonly fabricated with vacuum evaporation of low molar mass organic molecules; this is due to the employment of conducting PAN in the complex. On reflection of the I – V characteristics, light was emitted from the device above the bias voltage of 7 V, and the luminance of the device increased with the bias voltage (Fig. 1(b)). The maximum luminance of 1500 cd m^{-2} was observed at 11 V. As can be seen by comparison between Figs. 1(a) and (b), the luminance seems to increase linearly with injected charges. Turn-on response of the luminance of the device was very fast for our device. Although we could not measure its quantitative response time, the turn-on response was without doubt much faster than a second. We evidently confirmed flicker due to emission-on and off from the device when an ac bias voltage of 9 V was applied to the device at a frequency of 30 Hz. This indicates that the turn-on and off response should be faster than 30 ms. The response seems to

be comparable to the Al–quinolinium complex-based EL device to our naked eye. This behavior seems to be different from that of previously reported Ru complex-based devices. This indicates that the present emitting mechanism is not electrochemical but instead is that commonly observed for the EL device fabricated by vacuum-evaporation of organic molecules. Furthermore, the emission behavior did not vary after the first five turn-on and off cycles with 1 s intervals, giving further evidence that the mechanism is not electrochemical.

The electroluminescence (EL) spectrum of the device and photoluminescence (PL) spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ are shown in Fig. 1(c). The PL spectrum was measured for $\text{Ru}(\text{bpy})_3^{2+}$ in an aqueous solution. The EL spectrum was found to be almost identical to the PL spectrum, indicating that the red light was emitted from $\text{Ru}(\text{bpy})_3^{2+}$ in the DNA–PAN matrix. However, the emission peaks were found to red-shift from 610 nm for PL in the solution to 620 nm for device EL, and the EL spectrum was slightly broader than the PL. This is due to the electronic interaction between $\text{Ru}(\text{bpy})_3^{2+}$ molecules which increases as the separation between $\text{Ru}(\text{bpy})_3^{2+}$ molecules decreases.

As described in the introduction of this paper, the role of DNA for this device is interesting to estimate. The point of whether DNA is the electron transporter is not clear. We do not have any quantitative evidence that electrons pass through the DNA backbone. Taking into account the presence of electroactive $\text{Ru}(\text{bpy})_3^{2+}$ in the matrix and the very low conductivity ($<10^{-10} \text{ S cm}^{-1}$) of DNA film alone, electron transfer through $\text{Ru}(\text{bpy})_3^{2+}$ from the cathode is plausible in the present EL device. When poly(anilinesulfonic acid) (SPAN) was employed instead of DNA–PAN complex to fabricate the EL device, no emission was observed from the device even at a bias voltage of 11 V. This is due to the increase of ineffective current resulting from the decrease of recombination probability between holes and electrons at $\text{Ru}(\text{bpy})_3^{2+}$ in the complex by employing the more conductive SPAN as matrix. When poly(vinylsulfonic acid) (PVS) was employed instead of DNA, the PVS–PAN complex containing $\text{Ru}(\text{bpy})_3^{2+}$ solution was prepared in a similar manner to the DNA–PAN solution for EL device fabrication. The ITO glass electrode, however, shed the solution differently from the DNA–PAN complex solution, and it was difficult for us to prepare thin, smooth and homogeneous complex film on the electrode. The film surface was qualitatively confirmed by AFM, indicating that the DNA–PAN complex film on the ITO glass electrode was smooth and homogeneous. These results suggest that DNA seems to play some important role for at least EL device fabrication. These interpretations must be regarded as preliminary. Further analysis must be done to clarify the role of DNA as well as the EL mechanism of the device.

Acknowledgements

The authors express their appreciation to the Nippon Chemical Feed Co., Ltd for providing the salmon testes DNA sample.

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