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Journal of Photochemistry and Photobiology A: Chemistry 158 (2003) 215–218
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photoresponsive organic electroluminescent devices

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Received 18 April 2002; accepted 7 October 2002

Abstract

We have proposed novel photoresponsive green- and blue-emitting organic electroluminescent (EL) devices combining organic EL diodes with titanyl phthalocyanine as a photoconductive layer. By irradiating red and near-infrared (IR) lights to these devices, green and blue emissions were generated, respectively, well below the turn-on voltage. The results indicate that the devices act as an optical switch and up-converter. The EL response time using a laser pulse was about 300 μs. Above the turn-on voltage, enhancement of the EL intensities was observed with the light irradiation with the ratio of up to 10^4.

Keywords: Organic electroluminescent device; Organic photoconductor; Titanyl phthalocyanine; Optical switch; Light up-conversion; Light enhancement

1. Introduction

Organic electroluminescent (EL) devices have received considerable attention due to high potential for display applications [1–4]. In recent years, there has been growing interest in application of organic EL devices to advanced optoelectronic devices. Hiramoto et al. [5–7] have reported organic light transducers combining organic photoconductor (OPC) layers (photon to electron conversion) with organic EL diodes (electron to photon conversion). However, the devices needed to be driven at high applied voltage under vacuum and to use thick OPC layer (above 500 nm). In addition, optical switching response of the devices was on the order of seconds, too slow to be applied as optoelectronic devices.

Recently, we have proposed that a new type of the photoresponsive organic EL device including a thin OPC layer could be driven at low voltage under ambient condition [8]. Schematic structure of the photoresponsive organic EL device is shown in Fig. 1(a). In this device, a thin OPC layer was interposed between an organic EL diode and an indium-tin oxide (ITO) anode. By irradiating external light to the device, photocarriers are generated in the OPC layer and then the carriers are injected into the EL diode. As a result, the device exhibits the EL emission. We used titanyl phthalocyanine (TiOPc) for the OPC layer because this material had high quantum efficiency of photon–electron conversion [9]. The TiOPc film has a strong absorption band in the region from red to near-infrared (IR), while representing very weak absorption from 400 to 600 nm (Fig. 1(b)). So, it is reasonably considered that green and blue emissions from emissive materials, tris-(8-hydroxy quinoline) aluminum (Alq_3) and *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1-1′biphenyl-4,4′-diamine (α-NPD) for example, can be taken out from the ITO side efficiently without absorption in the OPC layer. In this paper, we report about new photoresponsive organic EL devices exhibiting green and blue emissions by red and near-IR light irradiation, respectively.

2. Experimental

A TiOPc layer was deposited on an ITO coated glass substrate. The green-emitting diode which consisted of *N*,*N*′-diphenyl-*N*,*N*′-di(*m*-tolyl)benzidine (TPD) as a hole transport layer and Alq_3 as an electron transport and emitting layer was constructed on the TiOPc layer. The blue-emitting diode which consisted of α-NPD as an hole transport and emitting layer and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine or BCP) as an electron transport and hole blocking layer [10] was constructed on the TiOPc layer. A thickness of each organic layer was same as 60 nm. Deposition was carried out at a pressure of $<2 \times 10^{-6}$ Torr. Deposition rate of each organic material was typically 0.3–0.7 nm/s. Finally, 150 nm thick magnesium and silver (10:1) was co-deposited as a cathode on the organic layers. The active area of the device was 4 mm^2.

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1010-6030/03/$ – see front matter
doi:10.1016/S1010-6030(03)00036-4

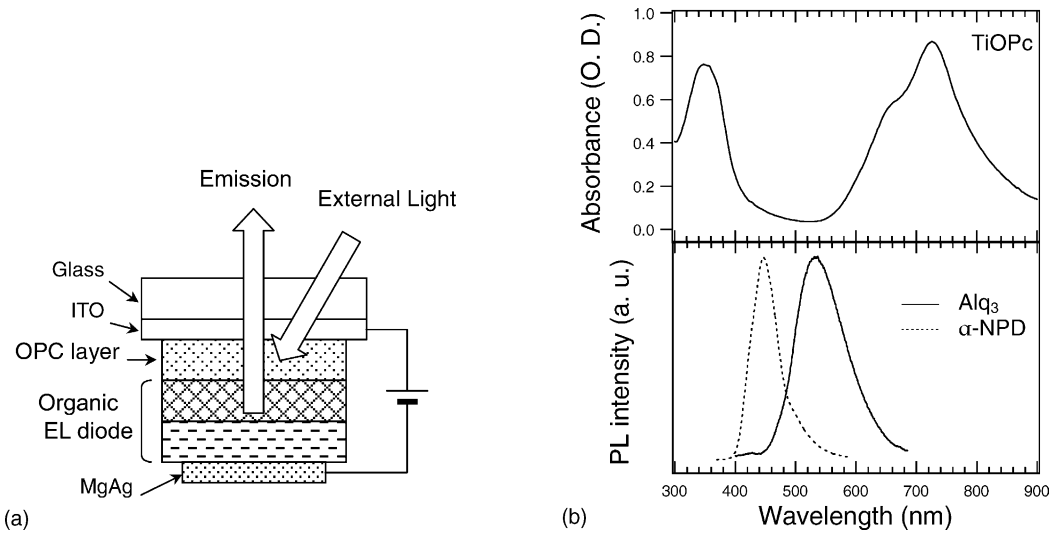

Fig. 1. (a) Schematic structure of the photoresponsive organic EL device; (b) absorption spectrum of 60 nm thick TiOPc film on a quartz substrate (upper panel) and PL spectra of Alq_3 and α-NPD films on quartz substrates (lower panel).

The luminance of the device was measured by the use of a luminance meter (Topcon BM-8) and the current–voltage (*I–V*) characteristics were measured with an electrometer (Keithley 2400). EL spectra of the device were measured utilizing a charge-coupled device multichannel detector equipped with a polychromator (Princeton Instruments). Red (650 nm) and near-IR (780 nm) lasers were used as incident lights to the green- and blue-emitting devices, respectively. The devices were irradiated from the side of the ITO anode by the laser beam with the power density of 50 mW/cm^2. The temporal evolution of the electroluminescence in response to a laser pulse was measured by a streak camera (Hamamatsu Photonics K.K.). A pulse generator (Stanford Research Systems DG535) triggered the streak camera as well as the lasers to generate square-shaped pulses to be injected into the device. The pulse width was 1 ms and the repetition frequency was 200 Hz. All measurements were carried out at room temperature in ambient air.

3. Results and discussion

Fig. 2(a) shows luminance–voltage (*L–V*) characteristics of the green-emitting device with and without red laser irradiation. Under non-irradiated condition, green emission was observed above 12 V and the luminance increased with increasing the applied voltage. When the device was irradiated by the red laser, the luminance was enhanced instantaneously and the turn-on voltage was lower by 9 V than that of the non-irradiated condition. Therefore, in the range of the lower voltage (between 3 and 12 V) the device acted as an optical switching/up-converter, which converts low-energy red light to high-energy green light ("optical switching/up-conversion" mode). Moreover, above 12 V the device exhibited enhancement of green emission with red

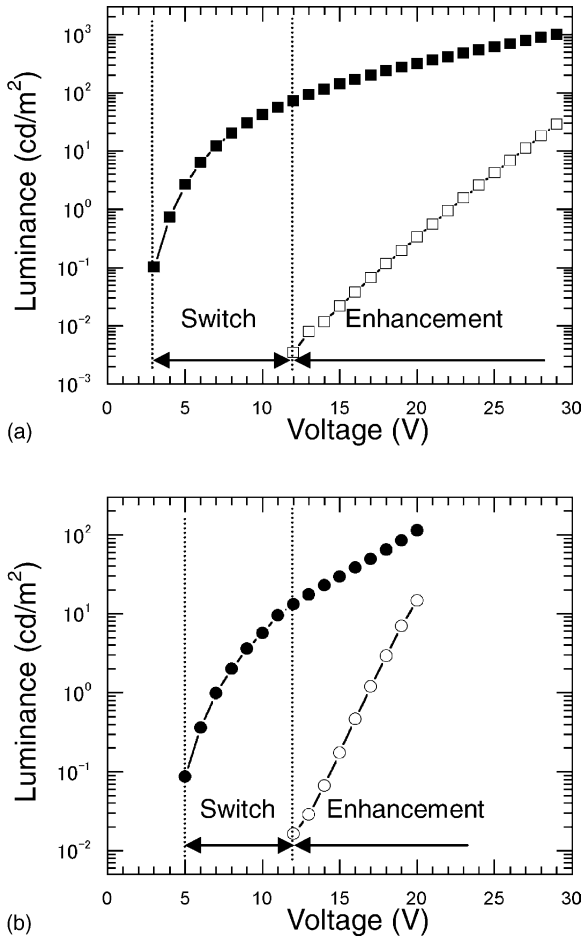

Fig. 2. *L–V* characteristics of the green (a) and blue (b) emitting devices under the non-irradiated (open) and irradiated (solid) conditions.

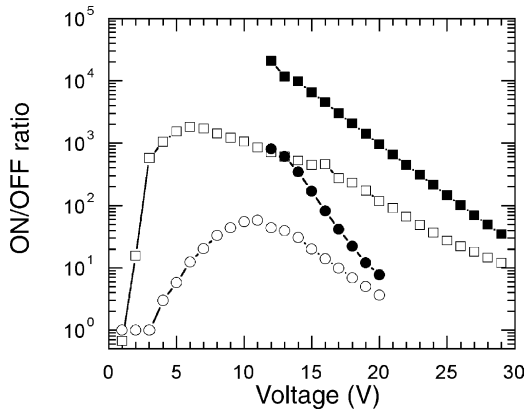

Fig. 3. Laser ON/OFF ratios of current and EL intensity. Squares represent the ratio of current (open) and EL intensity (solid) of the green-emitting device. Circles represent the ratio of current (open) and EL intensity (solid) of the blue-emitting device.

light irradiation ("light enhancement" mode). *L–V* characteristics of the blue-emitting device with and without near-IR laser irradiation are shown in Fig. 2(b). Between 5 and 12 V, the device acted as an optical switching device and up-converter from near-IR to blue. Above 12 V, the device exhibited enhancement of blue emission with near-IR light irradiation.

Fig. 3 shows laser ON/OFF ratios of current and EL intensity of the devices. Photocurrent of the green-emitting device was observed above 1 V. The laser ON/OFF ratio of current increased with applied voltage and reached 2×10^3 at 6 V. The current densities with and without laser irradiation at 6 V were 1.08×10^{-4} and 6×10^{-8} A/cm^2, respectively. Above 6 V the ratio decreased gradually with the voltage. The maximum of the laser ON/OFF ratio of the EL intensity was 2×10^4 at 12 V. The ratio decreased with increasing voltage. The current of the blue-emitting device was also enhanced by the laser irradiation above 3 V. The maximum of the laser ON/OFF ratio of the current was 60 at 11 V. The current densities with and without laser irradiation at 11 V were 1.02×10^{-3} and 1.75×10^{-5} A/cm^2, respectively. The maximum of the ratio of EL intensity reached about 10^3 at 12 V. Therefore, it is considered that both light appearance in the "optical switching/up-conversion" mode and light enhancement in the "light enhancement" mode are attributed to photocarrier generation in the TiOPc layer by laser irradiation.

EL efficiency of the green- and blue-emitting devices is shown in Table 1. The EL devices excluding TiOPc layers ("No TiOPc" in Table 1) were fabricated and evaluated, because these were compared with the photoresponsive EL devices. Since all compounds consisting of the "No TiOPc" devices, namely TPD, Alq_3, α-NPD and BCP, have no absorption in the region from red to near-IR, the "No TiOPc" devices did not exhibit any response by red or near-IR laser irradiation. The efficiency of the green- and blue-emitting devices was enhanced by laser irradiation. The result indicates that the TiOPc layer has photocarrier generation by

Table 1
EL efficiency of the photoresponsive EL devices and the corresponding devices without TiOPc layers

	EL efficiency[a] (cd/A)		
	Laser OFF	Laser ON	No TiOPc
Green	2.9	7.7	3.0[b]
Blue	0.2	0.9	0.7[c]

[a] Current density at 1 mA/cm^2.
[b] Device structure: ITO/TPD (60 nm)/Alq_3 (60 nm)/MgAg.
[c] Device structure: ITO/α-NPD (60 nm)/BCP (60 nm)/MgAg.

laser irradiation and then changes active as a hole injection layer. In particular, the efficiency of the green-emitting device was higher than that of the "No TiOPc" device. This result indicates that a new type of a high-performance EL device using external light was realized.

Fig. 4(a) shows typical EL spectra of the green-emitting device with and without red laser irradiation in the "light enhancement" mode. Under the non-irradiated condition,

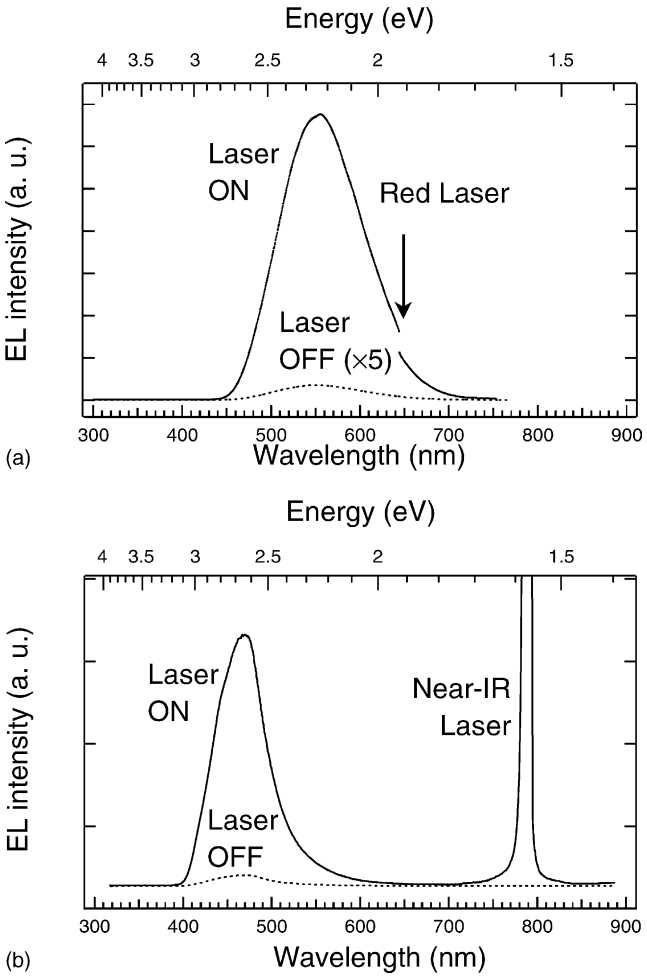

Fig. 4. EL spectra of the green (a) and blue (b) emitting devices under the non-irradiated (dashed line) and irradiated (solid line) conditions in the "light enhancement" mode. Data points around the red laser (650 nm) are omitted due to the strong scattering.

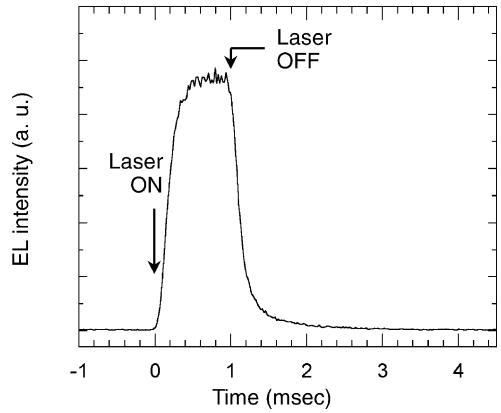

Fig. 5. EL response by the laser pulse in the "optical switching/up-conversion" mode.

green emission from Alq_3 was observed around 550 nm (2.3 eV). By red laser (1.9 eV) irradiation, the intensity of green emission was largely enhanced. In the case of the blue-emitting device, blue emission from α-NPD was observed around 470 nm (2.6 eV) under the non-irradiated condition (Fig. 4(b)). By near-IR laser (1.6 eV) irradiation, the intensity of blue emission was also enhanced largely. The great enhancement of emission is due to the high-efficient generation of photocarriers in the TiOPc layer and the enough injection of the carriers into the EL diode. For both the cases, there were no change in the shapes and peak positions of the spectra by laser irradiation. As a result, it was found that the devices exhibit the effect of photo-assisted light enhancement having no color change without and with laser irradiation. The emission spectra in the "optical switching/up-conversion" mode were also identical with those indicated in Fig. 4. Therefore, the energy gaps of red to green and near-IR to blue up-conversion were estimated to be 0.4 and 1.0 eV, respectively.

EL response of the blue-emitting device by near-IR laser pulse in the "optical switching/up-conversion" mode is shown in Fig. 5. Rise and decay times of temporal emissions, which were defined as the times between 10 and 90% of the saturated EL intensity, were 260 and 330 μs, respectively. These indicate that the photoresponse of this device was fast enough as the optical switching device. The device exhibited good reversibility of the switch. This fast response should be also caused by the high-efficient generation of photocarriers in the thinner OPC layer compared with the result by Hiramoto et al. [5–7]. Moreover, we confirmed that the optical switch only occurred in the laser-irradiated spot. Therefore, this photoresponsive EL device is considered as a promising candidate for an IR–visible image converter.

4. Conclusions

Novel photoresponsive organic EL devices combining organic EL diode with TiOPc photoconductive layer were successfully fabricated. These devices exhibited efficient up-conversions of red to green and near-IR to blue at the low drive voltages. The response time of optical switch for the laser pulse irradiation was about 300 μs. In addition, these emissions were significantly enhanced by light irradiation above the turn-on voltage.

Acknowledgements

We thank Dr. J.P. Ni, Dr. T. Tano, Dr. N. Tanigaki and Dr. S. Hoshino for helpful discussion.

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