Red organic electroluminescence devices with a reduced porphyrin compound, tetraphenylchlorin

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(Received 23 November 1998; accepted for publication 4 March 1999)

We constructed red organic electroluminescence (EL) devices with a reduced porphyrin compound, tetraphenylchlorin, that was doped at various concentrations (0.5, 1.7, and 3.7 wt%) within a tris(8-hydroxyquinoline) aluminum (Alq3) host layer. We measured their EL properties and found that all three devices emitted a red EL band at 660 nm with a width of 20 nm. Emission color of the 1.7 and 3.7 wt% devices was red (chromaticity coordinates $x=0.67$, $y=0.29$ and $x=0.78$, $y=0.21$) and the luminance maximum was 100 and 24 cdm^{-2}, respectively. The 0.5 wt% device emitted a green Alq3 EL band as well, and showed an increase in relative intensity of the Alq3 emission with increasing applied voltage. © *1999 American Institute of Physics.* [S0003-6951(99)01618-6]

One goal in the research on organic electroluminescence (EL) devices is to develop full-color displays. Thus far, several methods have been developed for obtaining blue, green, and red (BGR) color pixels.[1] Because the highest driving efficiency is attained by using self-emitting BGR pixels, it is important to develop light-emitting materials for each of these three colors. Although certain blue- and green-emitting materials have efficiencies sufficient for practical use,[2,3] red-emitting materials remain elusive. For example, the few reports on red materials involve 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM)[4] and europium chelate complexes.[5] Other recent reports on EL devices involve porphyrin compounds, such as tetraphenylporphine (TPP),[6] zinc-tetraphenylporphyrin (ZnTPP),[7] and platinum-octaethylporphyrin (PtOEP).[8] Because porphyrin compounds have many related compounds that have various molecular structures and electronic states, we searched these compounds for new red-emitting materials.

In this study, we used a chlorin compound, tetraphenylchlorin TPC (Fig. 1). Chlorin compounds belong to a class of reduced porphyrins in which at least one of the exo pyrrole double bonds is reduced by hydrogen. This reduction produces electronic states of chlorin that differ from those of corresponding ordinary porphyrins;[9,10] the most striking difference is the increased oscillator strength of the *Q*-band transition and the corresponding increased intensity of the (0–0) transition. However, the red emissive property is preserved, and for TPC, we found a sharp red photoluminescence (PL) band at ~660 nm (Fig. 2). This property makes this compound promising as a red-emitting EL material. Therefore, we fabricated organic EL devices using this material, and then measured their EL properties (emission color, maximum luminance, electroluminescence spectra, and current–voltage property).

Based on the construction of other porphyrin-based EL devices,[6–8] we constructed EL devices in which TPC molecules were doped within a tris(8-hydroxyquinoline) aluminum (Alq3) host layer. The spectral overlap between Alq3 emission and TPC absorption was favorable for Förster energy transfer from the host to the dopant. For three TPC concentrations (0.5, 1.7, 3.7 wt%), we fabricated EL devices (A, B, and C, respectively) whose four-layer structure was as follows: (1) 200-nm-thick indium tin oxide (ITO) electrode, (2) 50 nm holetransport layer of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD), (3) 50 nm emitting layer of TPC+Alq3, and (4) MgAg (10:1) electrode. The TPC was purchased from Tokyo Kasei and used without further purification. The ITO electrode (coated on glass substrates, and purchased from GEOMATEC Co., Ltd.) had a sheet resistance of 10 Ω/square and before use was ultrasonically washed with acetone, surface-active agent, pure water, and *iso*-propyl alco-

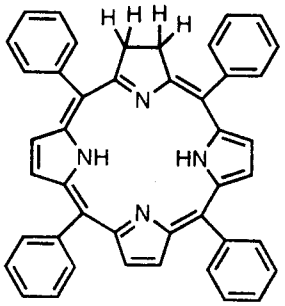

FIG. 1. Molecular structure of TPC.

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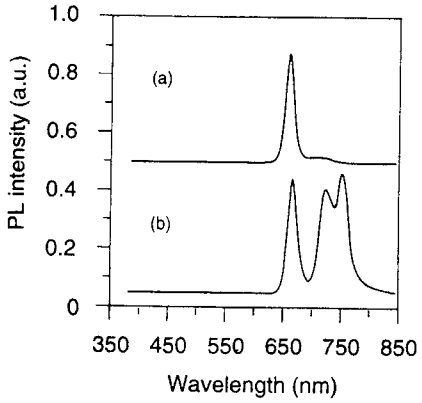

FIG. 2. Photoluminescence spectra of (a) TPC chloroform solution (5.0×10^{-6} mol/l) and (b) TPC vacuum-deposited film.

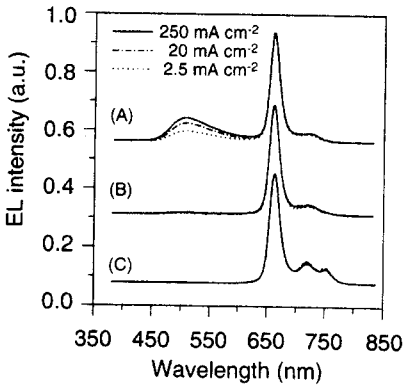

FIG. 3. Electroluminescence spectra of the EL devices at different current density. Spectra are normalized by the respective peak intensity at 660 nm.

hol, and then cleaned with a UV-O_3 cleaner. The two organic layers and metal electrode were deposited in a vacuum of 2×10^{-5} Torr. Emitting area was 2×2 mm^2. EL luminance was measured with a luminance meter (Minolta LS-110). EL spectra were measured with an optical multichannel photodetector (Photal IMUC-7000) whose wavelength sensitivity had been calibrated with a standard halogen lamp.

Table I shows color property and maximum luminance of each device. Although the emission color of device A was yellow, that of devices B and C was red. These color properties come from the differences among the EL spectra (Fig. 3). In all the spectra, there was a red luminescence band whose peak was 660 nm and width was 20 nm. The spectra for device A, however, also showed a green luminescence band due to Alq3 emission. This band caused the yellow color. For devices B and C, the green band was quenched, resulting in a red color. For device C, a weak far-red band occurred at around 750 nm as well. The wavelength of this weak band was invisible, and thus had no affect on the color property. The red band of device A was similar to the PL band of TPC monomer dissolved in chloroform solution [Fig. 2(a)], suggesting that the red band was emitted from monomer sites of the dopants. These results indicate that the emission origin of the 750 nm far-red band of device C differs from the monomer sites. For the doping concentrations studied here, the number of dopant molecules that had mutual interactions increased rapidly as the doping concentration was increased. Some of the dopant molecules might form *J* aggregate-like sites (including dimer, trimer, etc.) that emit fluorescence redder than that emitted by the monomers that have aggregation structures similar to porphyrin *J* aggregates.[11] The 750 nm EL band might be emitted from such aggregation sites. [For vacuum-deposited TPC films, the number of such sites may be higher, resulting in a stronger relative PL intensity of the far-red band, as seen in Fig. 2(b).]

The smaller maximum luminance of device C than that of device B indicates the existence of "concentrated quenching" phenomenon. This phenomenon might be interpreted as follows. Due to increased nonradiative processes by aggregation, some aggregate sites have lower emission efficiency than the monomer sites. Because we found that a TPC molecule has a large spectral overlap between $Q_x(0-0)$ emission band and $Q_x(0-0)$ absorption band, the energy transfer rate between the TPC molecules increases with increasing doping concentration. Consequently, a large number of the excited states of TPC molecules are trapped at the less emissive sites, resulting in a decrease in the total emission efficiency.

Figure 4 shows current versus voltage characteristics of the devices. Devices B and C required a larger driving voltage than did device A, indicating that either the electron injection barrier increases or the mobility of the injected electrons decreases. Figure 3 shows the dependence of the EL spectra on current density. For devices B and C, the spectra were similar. For device A, however, the relative intensity of the Alq3 emission increased with increasing voltage. Similar behavior was reported for a PtOEP-doped EL device that involved a red phosphorescence emission of the dopants.[8] For that device, the red emission saturates be-

TABLE I. Characteristics of the EL devices.

Device (TPC wt %)	Maximum luminance (cdm^{-2})	Chromaticity coordinates[a]	EL color
A (0.5)	1800	$x=0.45$[b] $y=0.43$[b]	yellow
B (1.7)	100	$x=0.67$ $y=0.29$	red
C (3.7)	24	$x=0.78$ $y=0.21$	red

[a]Commission internationale del'Eclairage (CIE) coordinates of the emitted light (1931).
[b]At 10 V.

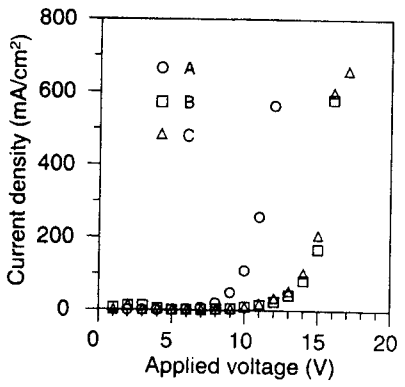

FIG. 4. Current density vs. voltage for the EL devices.

cause of its long lifetime $\sim 100\,\mu$s. For device A, however, such saturation cannot occur. For a doping concentration of 0.5 wt %, we estimated that the number of dopant sites in the ~ 5-nm-thick recombination zone[4] near the TPD/TPC:Alq3 interface is $\sim 5\times 10^{12}\,\mathrm{cm}^{-2}$. At a maximum driving current of $600\,\mathrm{mA\,cm}^{-2}$, the number of carriers is $4\times 10^{18}\,\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$. Therefore, even if all the carriers contribute to the excitation of dopant sites, the average excitation period per site is $\sim 1\,\mu$s. Because this period is much larger than TPC fluorescence lifetime (nanoseconds), saturation of TPC emission is impossible at that driving current. This means that, assuming a constant Förster energy transfer rate from the excited Alq3 sites to the TPC sites, the EL intensities of the Alq3 band and the TPC band maintain a constant ratio irrespective of applied voltage. Therefore, the relative increase in Alq3 emission requires alternative explanations.

Although experimental confirmation is needed, there are three possible explanations. First, the relative increase in the Alq3 emission may be due to a decrease in the fluorescence efficiency of the TPC sites caused by, for example, electric field-induced quenching.[12] Second, the energy transfer rate may decrease with increasing voltage. Third, portions of the dopants may be excited not by energy transfer but by charge recombination on their sites. Therefore, with increasing voltage, recombination on the Alq3 sites might increase more rapidly than that on the dopant sites because, compared with TPC, Alq3 has a higher lowest unoccupied molecular orbital level through which an electron is trapped on the site.

Although the bandwidth of the red band for the EL devices that we constructed is satisfactorily narrow for display applications, the peak wavelength of 660 nm is too red. Using other chlorin compounds, such as octaethylchlorins and ordinary chlorines, would significantly shorten the peak wavelength, thus increasing the luminance because spectral luminous efficiency increases rapidly with decreasing wavelength (e.g., efficiency of 0.061 at 660 nm would be 0.265 at 630 nm).

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