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Red electroluminescence and photoluminescence properties of a reduced porphyrin compound, tetraphenylchlorin

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Abstract

We report red PL and EL properties of a reduced porphyrin, tetraphenylchlorin (TPC). In monomer solution TPC emitted a red PL band at 655 nm. In solid mono-film TPC emitted a red PL band at 660 nm but it also emitted two far-red PL bands at 725 and 750 nm due to aggregated emission sites in the film. EL devices in which TPC were doped at concentrations of 1.6–3.7 wt.% within an Alq_3 host layer showed red EL color due to a 660-nm emission of TPC monomer with a width of 20 nm. The red-emitting devices using α-NPD as a hole-transport layer had maximum luminance higher than those using TPD did. Among the red devices, we obtained a maximum luminance of 520 cd/m^2 with chromaticity coordinates of $x = 0.620$ and $y = 0.31$.

Keywords: Organic electroluminescence diodes; Red emission; Tetraphenylchlorin; Reduced porphyrin

1. Introduction

One goal in the research on organic electroluminescence (EL) diodes is to develop full-color displays. For this goal, it is important to develop blue, green, and red light-emitting materials. Now, although certain blue- and green-emitting materials have properties sufficient for practical use [1,2], red-emitting materials remain elusive. Recently, some porphyrin compounds such as tetraphenylporphine (TPP) [3], zinc-tetraphenylporphyrin (ZnTPP) [4] and platinum-octaethylporphyrin (PtOEP) [5] have been known as red-emitting materials. Besides these compounds, there are many porphyrin-related compounds that have various molecular structures and electronic states. Therefore, it is significant to search such compounds for new red-emitting materials.

Among the many porphyrin-related compounds, chlorins (a class of reduced porphyrins in which at least one of the exo pyrrole double bonds is reduced by hydrogen [6]) are promising because they emit red photoluminescence (PL). In addition, because they are model compounds of the chlorophylls that play an important photofunction in the photosynthetic system [6,7], we have an interest in using chlorin compounds as EL materials. Therefore, in this work we investigated red-emitting EL and PL properties of a representative chlorin compound, tetraphenylchlorin (TPC, see Fig. 1), which is a reduced compound of TPP.

2. Experimental

We constructed EL devices in which TPC was doped within a tris(8-hydroxyquinoline) aluminum (Alq_3) host layer (Fig. 2). We used hole-transport materials of *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-[1,1′–biphenyl]-4,4′-diamine (TPD) or *N,N′*-diphenyl-*N,N′*-di(1-naphtyl)-1,1′biphenyl-4,4′-diamine (α-NPD). TPC was doped at various concentrations (0.5, 1.7 and 3.7 wt.% for TPD-based devices, and 1.6 and 3.2 wt.% for α-NPD-based devices). The TPC was purchased from Tokyo Kasei and used without further purification. The organic layers and metal electrode were deposited in a vacuum of 2×10^{-5} Torr. The emitting area was 2×2 mm^2.

3. Results and discussion

3.1. Photoluminescence and absorption of TPC

The photoluminescence and absorption spectra of TPC were measured to check basic optical properties (Figs. 3 and 4). In chloroform solution where TPC molecules were dissolved as monomers, TPC emitted a sharp red PL band at 655 nm with a weak far-red vibronic band at 690–750 nm

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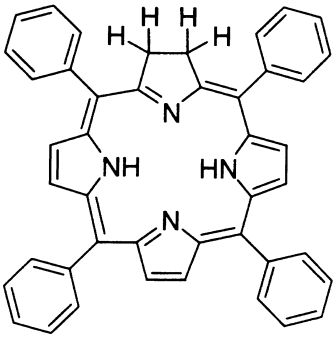

Fig. 1. Molecular structure of TPC.

(Fig. 3a). In a mono-film prepared by vacuum deposition, TPC emitted a similar sharp red PL band at 660 nm but it also emitted two far-red bands at 725 and 750 nm with intensities comparable to the 660-nm band (Fig. 3b). Because the mono-film was amorphous, it was probable that there were various TPC sites; some might form monomer-like sites and others might form aggregate-like sites (including dimer, trimer, etc.). We infer that the 660-nm emission was due to the monomer-like sites because its wavelength and shape are similar to those of monomer (Fig. 3a). We infer that the far-red emission was composed of two types: (1) vibronic band due to the monomer-like sites giving minor intensity, and (2) red-shifted fluorescence band due to the aggregate-like sites giving major intensity. We believe that red-shifted aggregate emission with a distinct peak (not like structureless excimer emission) is possible if there exist J-aggregate-like sites that have smaller dipole-allowed transition energy than monomer does. In fact, there are examples of porphyrin J-aggregates for tetrasulfophenylporphyrin [8] and chlorophyll [9]. Therefore, we believe that J-aggregate-like sites existed in the TPC mono-film.

Both chloroform solution and the mono-film had absorption bands called as Q-band [6] in 500–700 nm region (Fig. 4a,b). This region covered EL emission region of Alq_3 (Fig. 4c). This spectral overlap was favorable for Förster energy transfer from Alq_3 to TPC.

3.2. EL properties of the devices

The 655-nm emitting property of TPC monomer (Fig. 3a) was promising for a red-emitting EL material. Therefore, we constructed the EL devices and measured their EL proper-

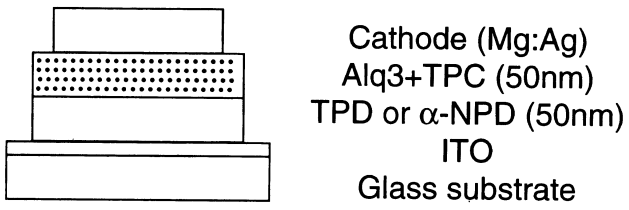

Fig. 2. EL device structure with a TPC-doped layer.

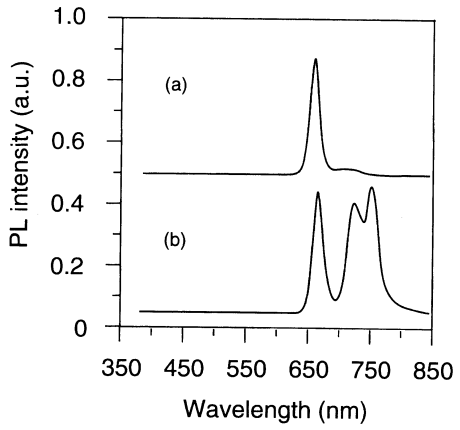

Fig. 3. Photoluminescence spectra of (a) TPC chloroform solution (5.0×10^{-6} mol/l) and (b) mono-TPC film prepared by vacuum-deposition.

ties. Table 1 shows color property and maximum luminance of each device. Although the emission color of the 0.5 wt.% device was yellow, that of the other devices was red. Fig. 5 shows EL spectra of the TPD-based devices. In all the spectra, there was a red luminescence band whose peak was 660 nm and width was 20 nm. The spectrum for the 0.5 wt.% device, however, also showed a green luminescence band due to Alq_3 emission. This band caused the yellow color. For the 1.7 and 3.7 wt.% devices, the green band was quenched, resulting in a red color. The red band of the 0.5 and 1.7 wt.% device was similar to the PL band of TPC monomer dissolved in chloroform solution (Fig. 3a), suggesting that the red band was emitted from monomer sites of the dopants. For the 3.7 wt.% device, a weak far-red band occurred at around 750 nm as well. 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 the aggregate-like sites (including dimer, trimer, etc.), and therefore the far-red EL bands

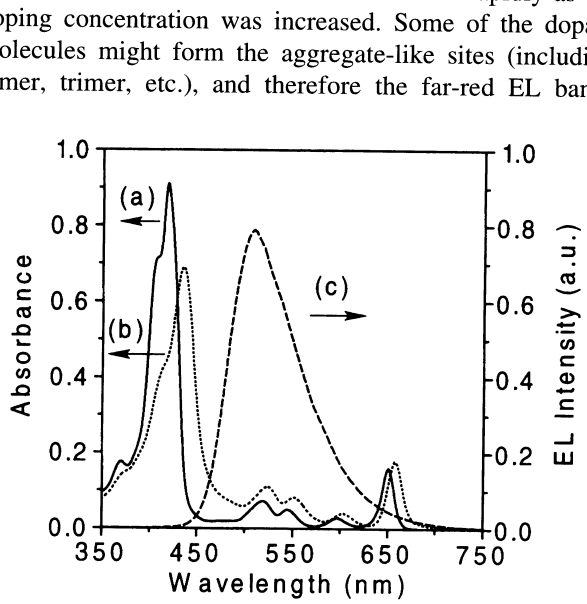

Fig. 4. Absorption spectra of (a) TPC chloroform solution and (b) mono-TPC film. (c) Electroluminescence spectrum of an ITO/TPD/Alq_3/MgAg device.

Table 1
Maximum lu

TPC wt.% (h
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1.7 (TPD)
3.7 (TPD)
1.6 (α-NPD)
3.2 (α -NPD

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Table 1
Maximum luminance and color property of the type A devices

TPC wt.% (hole-transport material)	Maximum luminance (cd/m^2)	Driving voltage (V)	Chromaticity coordinates[a]	EL color
0.5 (TPD)	1800	12	$x = 0.45$[b], $y = 0.43$[b]	Yellow
1.7 (TPD)	100	16	$x = 0.67$, $y = 0.29$	Red
3.7 (TPD)	24	17	$x = 0.78$, $y = 0.21$	Red
1.6 (α-NPD)	520	12	$x = 0.62$, $y = 0.31$	Red
3.2 (α -NPD)	70	13	$x = 0.76$, $y = 0.22$	Red

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

might be emitted from such aggregation sites. This interpretation is based on the fact that the far-red EL wavelengths corresponded to the far-red PL wavelengths of the mono-film. (For TPC mono-film, the number of such sites may be higher, resulting in a stronger relative PL intensity of the far-red band, as seen in Fig. 3b.) The α-NPD-based devices also involved little or no Alq_3 emission, resulting in the red EL color (Table 1).

In TPD-based devices, maximum luminance of the 3.7 wt.% device was smaller than that of the 1.7 wt.% device (Table 1). This indicates the existence of concentration quenching phenomenon. (We see the same phenomenon for the α-NPD-based devices). This phenomenon might be interpreted as follows: due to increased non-radiative processes by aggregation, some aggregate sites have lower emission efficiency than the monomer sites. Because TPC monomer has a large spectral overlap between emission band and absorption band at ~655 nm (see Figs. 3a and 4a), the energy transfer rate between the TPC molecules increases with increasing doping concentration. In addition, the number of the aggregate sites increases with increasing doping concentration. Consequently, a large number of the excited states of TPC molecules are trapped at the less emissive aggregate sites, resulting in a decrease in the total emission efficiency.

For the devices with similar doping concentrations, the α-NPD-based devices had higher maximum luminances than the TPD-based devices did (Table 1). This might be related to the fact that the α-NPD-based devices required smaller driving voltage than the TPD-based devices (Figs. 6 and 7). However, now we do not have a clear explanation for the luminance improvement when using α-NPD, and further investigation is necessary for this issue.

The bandwidth of the red EL band (20 nm) is satisfactorily narrow for display applications. However, luminance is

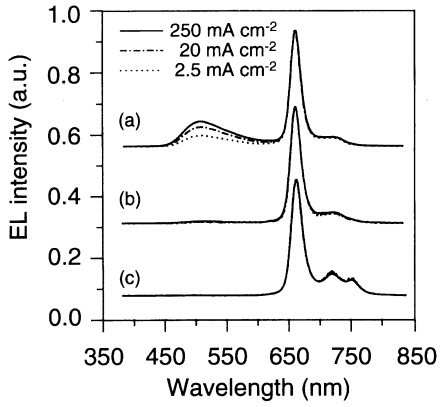

Fig. 5. Electroluminescence spectra of the TPD-based devices with doping concentration of (a) 0.5, (b) 1.7 and (c) 3.7 wt.% at different current density. Spectra are normalized by the respective peak intensity at 660 nm.

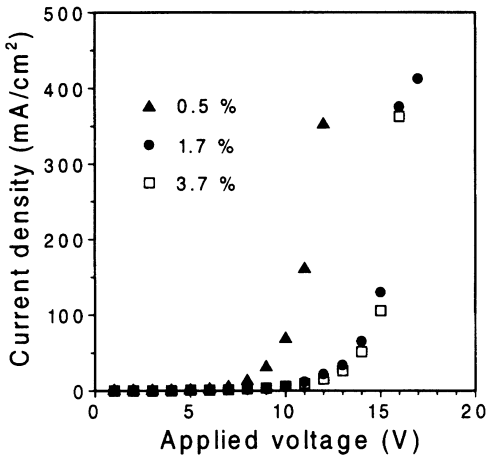

Fig. 6. Current density vs. voltage for the TPD-based devices with various doping concentrations.

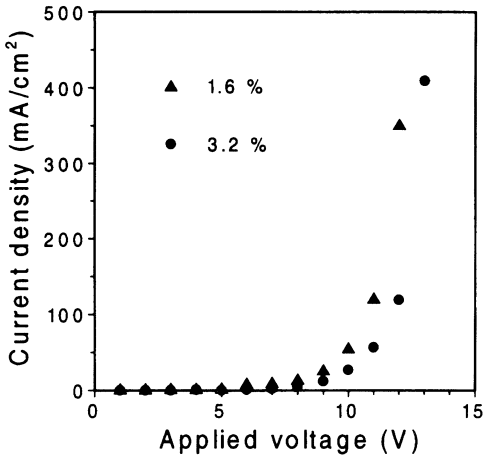

Fig. 7. Current density vs. voltage for the α-NPD-based devices with various doping concentrations.

not sufficient yet. For luminance improvement, shortening the peak wavelength is a significant way because spectral luminous efficiency increases rapidly with decreasing wavelength (e.g. luminous efficiency of 0.061 at 660 nm would be 0.265 at 630 nm). For this purpose, using other chlorin compounds, such as octaethylchlorins and ordinary chlorins, would be useful.

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