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Electroluminescence Properties of Three-Layered Organic Light-Emitting Diodes with a Layer of Tetraphenylchlorin or Tetraphenylporphine

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We constructed two organic electroluminescence (EL) devices that had a light-emitting layer of tetraphenylchlorin (TPC) or tetraphenylporphine (TPP), which was inserted between a hole transport layer of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) and an electron transport layer of tris(8-hydroxyquinoline) aluminum (Alq_3). The TPC device emitted a far-red EL band at around 750 nm, which we ascribed to emission from aggregated TPC sites. The TPP device emitted a red EL band at 660 nm and a far-red EL band at 720 nm, which we ascribed to emission from monomer-like TPP sites. Both devices also emitted green EL bands due to Alq_3 emission although the emission was partly filtered off by absorption of the TPC or TPP layer.

KEYWORDS: organic electroluminescence diode, porphyrin compounds, tetraphenylchlorin, tetraphenylporphine, red and far-red emission

A double-layered organic electroluminescence diode (OELD) with high emission efficiency and low-voltage operation, first demonstrated by Tang and Vanslyke,[1] inspired a large amount of research on OELD device structures, materials, and fabrication techniques. In OELD devices, the light-emitting layer is a key element. There exist several prevailing methods to constitute the layer through the arrangement of light-emitting materials. A basic method is to use a layer of quinoline-metal complexes such as tris(8-hydroxyquinoline) aluminum (Alq_3) which works as both a light-emitting layer and an electron transport layer.[1] A practical method which is conventionally used is to dope luminophore molecules within a layer of host materials such as quinoline-metal complexes.[2] However, the doping process requires simultaneous control of evaporation rates of host material and luminous material. In addition to these methods, there is a method of inserting a light-emitting layer composed of mono-component material between a hole transport layer and an electron transport layer, constituting a three-layered structure.[3] Compared with doping material, the use of mono-component material has a merit in the fabrication of thin layers because it needs only a single evaporation process which is free from the strict control of the evaporation rate. At the same time, however, the concentration of molecules in the layer induces, in many cases, a decrease of the fluorescence emission efficiency and/or a change in the emission color. Hence, it is necessary to check if the mono-component material is suitable as a light-emitting layer.

In a previous letter[4] we reported a red-emitting OELD using a reduced porphyrin compound tetraphenylchlorin (TPC, see inset of Fig. 1) doped in an Alq_3 layer. Other researchers also reported red-emitting OELDs using porphyrin compounds, such as tetraphenylporphine (TPP, see inset of Fig. 2),[5] zinc-tetraphenylporphyrin (ZnTPP)[6] and platinum-octaethylporphyrin (PtOEP)[7] doped in quinoline host layers. Because of the reason mentioned above, we were interested in the electroluminescence (EL) properties of three-layered structures that involved a mono-component porphyrin layer. In this study, we examined two metal-free porphyrin compounds, TPC and TPP.

We constructed three-layered EL devices as follows. First, an indium-tin-oxide (ITO) electrode with a sheet resistance of 10 Ω/square (coated on glass substrates, and purchased from GEOMATEC Co., Ltd.) was ultrasonically washed with acetone, a surface-active agent, pure water, and isopropyl alcohol, and then cleaned with a UV-O_3 cleaner. Then, in a vacuum of 2×10^{-5} Torr we deposited three organic layers: (1) a 40-nm-thick layer of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD), (2) a 40-nm-thick layer of TPC (or TPP), and (3) a 30-nm-thick layer of Alq_3. Finally, we deposited an MgAg (10 : 1) electrode. The TPC and TPP (chlorin-free grade) were purchased from Tokyo Kasei and used without further purification. The emitting area was $2 \times 2\,mm^2$. The EL luminance was measured with a luminance meter (Minolta LS-110). EL spectra were measured with an optical multichannel photodetector (Photal IMUC-7000).

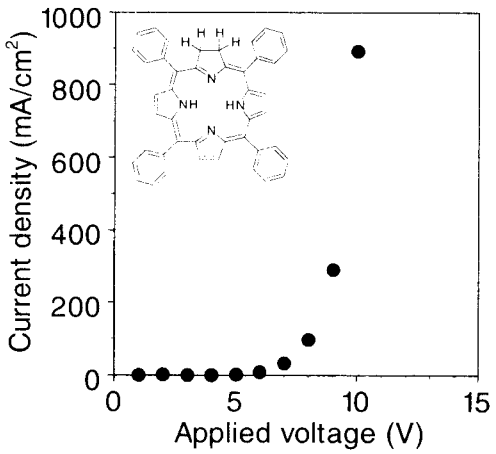

Fig. 1. Current-voltage property of an ITO/TPD/TPC/Alq_3/MgAg device. Molecular structure of TPC is shown in the inset.

Figures 1 and 2 show current-voltage properties of the devices. With increasing voltage, the current increased nonlinearly at more than 6 V for the TPC device (Fig. 1) and 5 V for the TPP device (Fig. 2). Then, the devices emitted EL of which the luminance was proportional to the current. The maximum luminance was 1600 cd/m^2 at 10 V for the TPC device and 1700 cd/m^2 at 10 V for the TPP device.

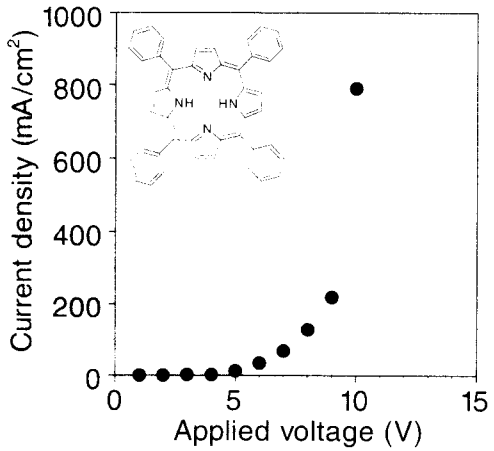

Fig. 2. Current-voltage property of an ITO/TPD/TPP/Alq_3/MgAg device. Molecular structure of TPP is shown in the inset.

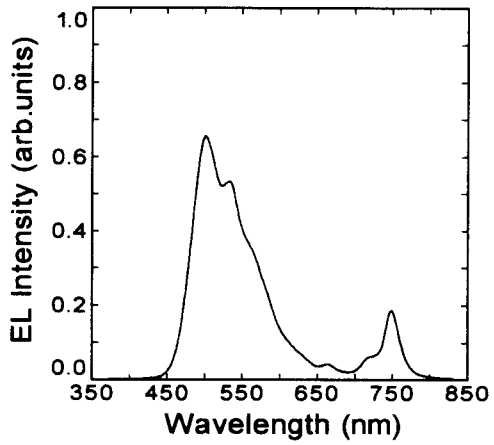

Fig. 3. Electroluminescence spectrum of the TPC device.

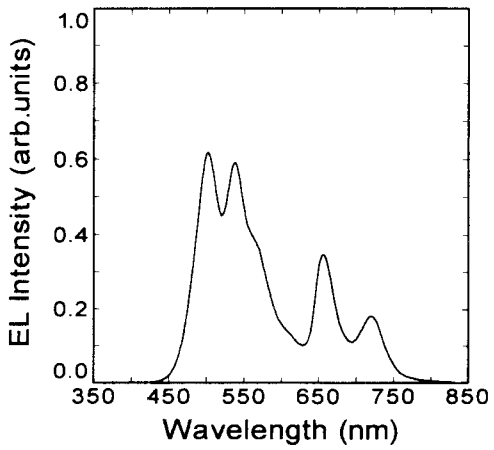

Fig. 4. Electroluminescence spectrum of the TPP device.

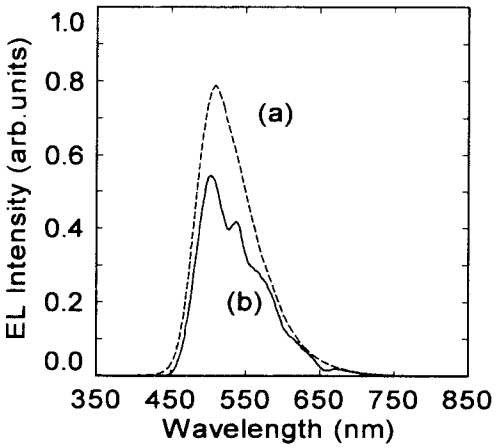

Fig. 5. (a) Electroluminescence spectrum of an ITO/TPD/Alq_3/MgAg device. (b) Simulated Alq_3 emission spectrum transmitted through a 40-nm-thick TPC layer.

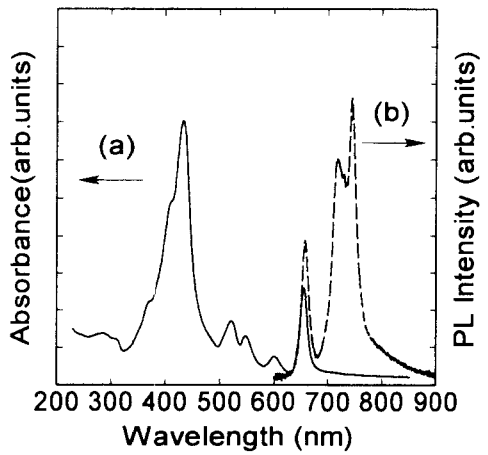

Fig. 6. (a) Absorption spectrum and (b) photoluminescence spectrum of a mono-TPC layer prepared by vacuum-deposition.

Both devices emitted green EL bands (450–630 nm) due to Alq_3 emission (Figs. 3 and 4). The devices also emitted red and far-red EL bands due to TPC emission (650–800 nm, Fig. 3) or TPP emission (630–800 nm, Fig. 4).

The existence of the Alq_3 emission is interpreted as follows. Because TPC and TPP are considered to be hole transport materials, the injected holes reached the TPC (or TPP)/Alq_3 interface. These holes were injected into the Alq_3 layer, and charge recombination occurred on Alq_3 sites. The green EL band apparently had structures (Figs. 3 and 4) which were different from the Alq_3 emission of an ITO/TPD/Alq_3/MgAg device [Fig. 5(a)]. These structures can be explained by a filter effect of the TPC and TPP layers that have complex absorption spectra in the Alq_3 emission region [Figs. 6(a) and 7(a)]. We simulated an Alq_3 emission spectrum transmitted through a 40-nm-thick TPC layer [Fig. 5(b)], for example, which was in good agreement with the green EL band of the TPC device (Fig. 3).

For the red and far-red EL bands, there are three possible mechanisms. First, electrons were injected into the TPC (or TPP) layer, and charge recombination on TPC (or TPP) sites occurred. Second, because Alq_3 emission and TPC (or TPP) absorption had a spectral overlap [see Figs. 5(a) and 6(a) for TPC and Figs. 5(a) and 7(a) for TPP], Förster energy transfer from excited Alq_3 sites to TPC (or TPP) sites occurred within the interface zone whose width was within the limit distance of dipole-dipole interaction (several nanometers), and then the TPC (or TPP) sites emitted photoluminescence. Third, the TPC (or TPP) layer absorbed Alq_3 emission, and the TPC (or TPP) layer emitted photoluminescence. The latter two processes always exist whenever Alq_3 emission occurs at the TPC (or TPP)/Alq_3 interface.

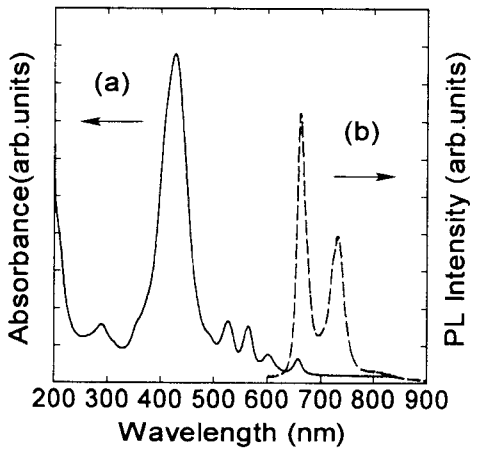

Fig. 7. (a) Absorption spectrum and (b) photoluminescence spectrum of a mono-TPP layer prepared by vacuum-deposition.

The existence of the first process in the TPC device is suggested by the finding that the EL spectrum involved a weaker red EL band at 660 nm than the photoluminescence (PL) spectrum of the mono-TPC layer did [see Figs. 3 and 6(b)]. Because the TPC layer was amorphous, we believe that the layer involved both monomer-like sites and aggregate sites. We believe that the 660 nm emission was due to monomer-like sites and the 750 nm emission was due to aggregate sites.[4] When these sites were excited electronically, because the aggregate sites had an excited level lower than the monomer sites,[8] it is probable that the charge recombination on the aggregate sites occurred dominantly and therefore, the EL spectrum involved more aggregate-emission than the PL spectrum did.

The TPP device involved red and far-red EL bands (Fig. 4), similar to that of the corresponding doping-device[5] from which monomer fluorescence was emitted. In addition, the PL spectrum of the TPP layer [Fig. 7(b)] was similar to that of the monomer in solution.[9] These findings suggest that, in the TPP layer, monomer-like sites were dominant.

Here, we discuss the emission efficiency of mono-component materials as compared with doped materials. When using mono-component material, concentration quenching is a severe problem. Doping luminophore molecules in a host material is a way to reduce such a quenching. At the same time, however, the number of dopant molecules within the recombination zone decreases with decreasing doping concentration. In the simplest estimation, the total EL efficiency of the luminophore material would be determined by a product of the doping concentration and the fluorescence quantum efficiency. Therefore, it is significant to compare the fluorescence quantum efficiency of the mono-component material with that of the monomer material. In our preliminary experiment using a backward fluorescence measurement configuration,[10] we found that the PL emission efficiency of a TPC film was ~1/20 times that of the TPC monomer in chloroform solution. Because the PL quantum efficiency of the TPC monomer is 0.26,[11] that of the TPC film is estimated to be 0.013. Also, we found that the PL emission efficiency of a TPP film was ~5 times that of a TPC film. Therefore, the PL quantum efficiency of the TPP film is estimated to be 0.065, which is half of that of the TPP monomer (0.13).[11] These findings suggest that concentration quenching is not a fatal disadvantage for these materials, especially for TPP, when the materials are used in three-layered devices.

For practical application, the 660 nm emission of the TPP device is attractive for a red OELD if the Alq_3 emission can be quenched. For this purpose, inserting a hole-blocking layer[12,13] between the Alq_3 layer and the TPP layer may be promising because it would reduce recombination within the Alq_3 layer and promote recombination within the TPP layer. The 750 nm emission of the TPC device covers the sensitivity region of the organic photoconductors (OPCs) based on phthalocyanine (Pc) materials such as H_2Pc and TiOPc. This property might be useful for a light-emitting diode (LED) printer head in combination with these OPCs. For this purpose, it may also be promising to insert a hole-blocking layer for suppressing the Alq_3 emission and promoting the TPC emission.

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