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Exciplex Emission in an Organic Electroluminescent Device Using Electron-transporting 1,3,5-Tris(4-tert-butylphenyl-1,3,4-oxadiazolyl)benzene and Hole-transporting N,N′-bis(3-methylphenyl)-N,N′-diphenyl-[1,1′-biphenyl]-4,4′-diamine

Hiromitsu Ogawa [a], Ryoji Okuda [a] & Yasuhiko Shirota [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, 565, Japan

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Exciplex Emission in an Organic Electroluminescent Device Using Electron-transporting 1,3,5-Tris(4-*tert*-butylphenyl-1,3,4-oxadiazolyl)benzene and Hole-transporting *N*,*N*'-bis(3-methylphenyl)-*N*,*N*'-diphenyl-[1,1'-biphenyl]-4,4'-diamine

HIROMITSU OGAWA, RYOJI OKUDA, AND YASUHIKO SHIROTA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

Exciplex formation at the organic solid-state interface in an organic electroluminescent device has been studied. A new multilayer device consisting of the electron-transport layer of 1,3,5-tris(4-*tert*-butylphenyl-1,3,4-oxiadiazolyl)benzene (TPOB) and double hole-transport layers of 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA) and *N*,*N*'-bis-(3-methylphenyl)-*N*,*N*'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (TPD) sandwiched between the electrodes of an alloy of magnesium and silver and indium tin oxide (ITO) emitted bright bluish-green light resulting from the exciplex formed at the interface between TPOB and TPD. The exciplex formation is evidenced by the measurement of the photoluminescence spectra of spin-coated films of TPOB, TPD, and a mixture of TPOB and TPD and their photoluminescence lifetimes.

Keywords: organic electroluminescent devices, multilayer device, amorphous molecular material, exciplex emission

INTRODUCTION

Organic electroluminescent (EL) devices have attracted a great deal of attention due to their potential application to full-color flat-panel displays. There have been extensive studies on organic EL devices using both low molecular-weight organic materials and polymers[1-2]. Generally, layered devices consisting of charge-transport and emitting layers seem to be preferable to a single-layer device using an emitting material alone in order to achieve high performances in organic EL devices. This is because a suitable combination of charge-transport and emitting materials in layered devices reduces the energy barrier for the injection of charge carriers from the electrodes, leading to better balance in the

number of injected holes and electrons. Therefore, it is necessary to develop charge-transport materials as well as emitting materials.

We have proposed "starburst molecule based on π-electron systems" as a new concept for the molecular design of photo- and electro-active amorphous molecular materials[3-5]. Based on this concept, we have created several novel families of amorphous molecular materials with high glass-transition temperatures that function as good charge-transport materials in organic EL devices. They include 4,4'4''-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA)[3,6-9], 4,4'4''-tris(1-naphthylphenylamino)triphenylamine (1-TNATA)[9], 4,4',4''-tris(2-naphthylphenylamino)triphenylamine (2-TNATA)[9], and 4,4'4''-tris[bis(4'-*tert*-butylbiphenyl-4-yl)amino]triphenylamine (*t*-Bu-TBATA)[10], 4,4'4''-tri(*N*-carbazolyl)triphenylamine (TCTA)[7,9,10], 1,3,5-tris[4-(3-methylphenylphenylamino)phenyl]benzene (*m*-MTDAPB)[5,8], and 1,3,5-tris[*N*-(4-diphenylaminophenyl)phenylamino]benzene (*p*-DPA-TDAB)[11], which function as hole-transport materials, and 1,3,5-tris(4-*tert*-butylphenyl-1,3,4-oxadiazolyl)benzene (TPOB)[9], which functions as an electron-transport material. In addition, we have shown that the multilayer device consisting of double hole-transport layers and an emitting layer exhibits high performances, significantly enhancing the durability of the device[6-10]. *m*-MTDATA functions as an excellent material for use in the hole-transport layer in contact with the ITO electrode in multilayer organic EL devices consisting of double hole-transport layers and an emitting layer.

In the layered organic EL devices, exciplex formation at the interface between the hole-transport layer and the electron-transport layer are suggested to take place for certain combinations of materials. However, there have been few reports describing in detail exciplex formation at the solid state interface in organic EL devices.

We report here exciplex formation at the interface between the electron-transport layer of TPOB and the hole-transport layer of *N*,*N*'-bis(3-methylphenyl)-*N*,*N*'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (TPD) in an organic EL device. A new multilayer organic EL device consisting of an electron-transport layer of TPOB and double hole-transport layers of *m*-MTDATA and TPD sandwiched between the electrodes of an alloy of magnesium and silver and indium tin oxide (ITO) was fabricated, which emitted bright bluish-green light originating from the exciplex formed at the interface between TPOB and TPD. The formation of the exciplex was evidenced by the

measurement of the photoluminescence spectra of spin-coated films of TPOB, TPD, and a mixture of TPOB and TPD and their photoluminescence lifetimes.

EXPERIMENTAL

A multilayer organic EL device was fabricated by successive vacuum deposition of the organic materials onto an ITO-coated glass substrate at a deposition rate of 2-3 $Å\,s^{-1}$ at 10^{-5} Torr. Then an alloy of magnesium and silver (ca. 10:1 in volume ratio) was deposited onto the organic layer by simultaneous evaporation from two separate sources. The emitting layer was about 4 mm^2. Organic thin films for the measurements of photoluminescence spectra and fluorescence lifetimes were prepared by spin coating from a benzene solution containing an equimolar amount of TPOB and TPD (each 5 x 10^{-3} mol dm^{-3}) onto a quartz glass substrate. Current-voltage-luminance characteristics for the organic EL devices were measured with an electrometer (Advantest TR6143) and a luminance meter (Minolta LS-100). The electroluminescence and photoluminescence spectra were taken on a fluorescence spectrophotometer (Hitachi F-4500). The time-resolved photoluminescence decay measurement was carried out by using the single photon counting technique with a time-resolved spectrofluorometer (Horiba NAES-1100).

RESULTS AND DISCUSSION

Fig. 1 shows the structure of the organic EL device fabricated together with the structures of the materials used in the present study.The device showed rectification behavior and emitted bright bluish-green light when a positive voltage was applied to the ITO electrode.

Fig. 2 shows the electroluminescence (EL) spectrum for the device together with the photoluminescence (PL) spectra of the spin-coated films of TPD, TPOB, and a mixture of TPOB and TPD. The TPOB solid film shows fluorescence with a peak at 370 nm. The weak fluorescence with a peak at ca. 510 nm observed for the TPOB solid film is suggested to result from an excimer. The EL spectrum, which is different from the PL spectra of the TPOB and TPD films, shows a strong peak at 510 nm together with a much weaker peak at ca. 410 nm. The EL spectrum for the device was in good agreement with the PL spectrum of a spin-coated film of an equimolar mixture of TPOB

and TPD. It is suggested that the EL with a peak at 510 nm originates from the exciplex formed at the interface between the hole-transport layer of TPD and electron-transport layer of TPOB. The emission with a peak at ca. 410 nm is attributed to the one resulting from TPD.

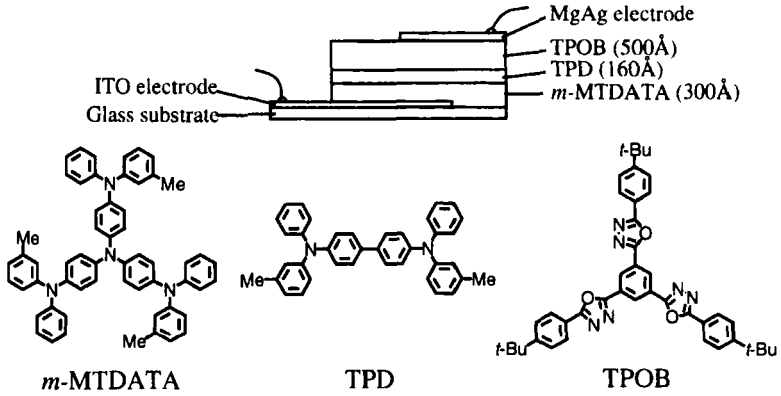

FIGURE 1 Side view of the device and materials used.

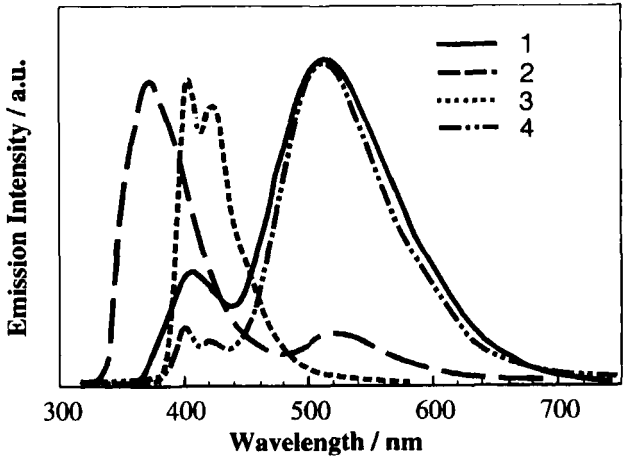

FIGURE 2 Electroluminescence spectrum of the device (1) and photoluminescence spectra of the films of TPOB (2), TPD (3), and a TPOB:TPD mixture (4).

The exciplex formation was further confirmed by the measurement of fluorescence lifetimes of the spin-coated films of TPOB, TPD, and the mixture

of TPOB and TPD. Whereas the time-resolved photoluminescence decay curves monitored at 370 and 400 nm for TPOB and TPD, respectively, were analyzed by single exponential decay, that for the mixture of TPOB and TPD monitored at 500 nm was analyzed as involving two components in appearance. The fluorescence lifetimes of the TPOB and TPD films were determined to be 3.9 and 7.6 ns, respectively (excitation wavelength : 300 nm, monitored at 370 and 400 nm for TPOB and TPD). By contrast, the fluorescence lifetimes of the two components for the mixture of TPOB and TPD were much longer, being 4.7×10^1 (35 %) and 1.3×10^2 ns (65 %) .

Consideration of the energy levels of TPOB and TPD suggests that the energy barrier in the hole injection from the TPD layer into the TPOB layer is higher than that in the electron injection from the TPOB layer into the TPD layer in the organic EL device. It is therefore suggested that the exciplex is formed by the interaction between TPD in the excited singlet state and TPOB in the ground state. The result that the exciplex emission is accompanied by the emission resulting from TPD is in support of this mechanism.

Fig. 3 shows the luminance versus applied voltage characteristics and the luminance versus injected current density characteristics for the device.

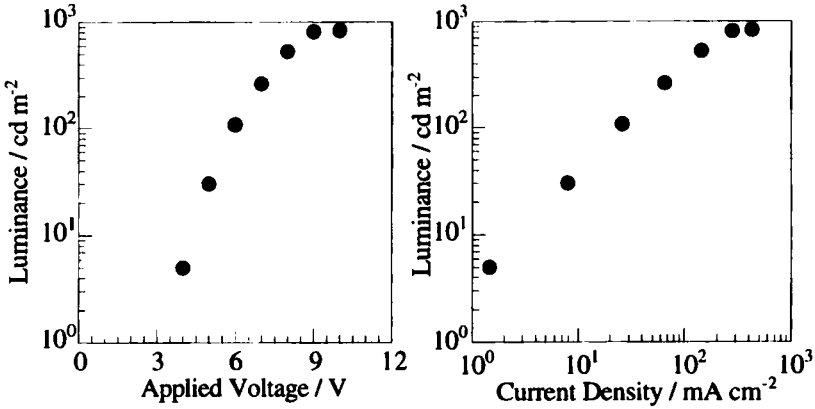

FIGURE 3 Luminance versus appled voltage and luminace versus current density characteristics of the device.

The emission with a luminance over 1 cd m^{-2} started at a driving voltage of 4 V, and a maximum luminance of 840 cd m^{-2} was obtained at 10 V. The luminous efficiency and the external quantum efficiency at 300 cd m^{-2} (applied voltage 7.1 V, injected current density 73.5 mA cm^{-2}) were 0.17 lm W^{-1} and 0.16 %, respectively.

Generally, the exciplex emission spectrum varies with the ionization potential of the electron donor for a fixed electron acceptor. It is expected that the emission color can be tuned by changing the ionization potential of the hole-transport material in organic EL devices using TPOB as an electron-transport layer.

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