

# Exciplex emission in bilayer Light-emitting device

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## Abstract

The bilayer organic light-emitting diode using Al(DBM)<sub>3</sub> (DBM=Dibenzoylmethane) as an emitting material and poly(N-vinylcarbazole) (PVK) as hole-transport material, emitted bright blue-green light instead of blue light. The blue-green emission is attributed to exciplex formation at the solid interface between Al(DBM)<sub>3</sub> and the hole-transport material. The exciplex formation was evidenced by the measurement of the photoluminescence spectra and lifetimes of Al(DBM)<sub>3</sub>, PVK and an equimolar amount of mixture of Al(DBM)<sub>3</sub> and PVK.

## 1. Introduction

Low molecular-weight materials based light-emitting devices have become a topic of great interest since the report of electroluminescent (EL) properties in aluminum tris-(8-hydroxyquinoline) (Alq<sub>3</sub>) [1]. A large variety of low molecular-weight materials have been shown to exhibit EL properties. For example, azomethine-zinc complexes [2] showed blue or ultraviolet emission, 3- or 5-hydroxyflavone-metal complexes [3] showed yellow emission, bis(4-hydroxyacridinato) zinc(ZnAc<sub>2</sub>) [4] and 5,10,15,20-tetraphenylporphyrinato zinc (ZnTPP) [4] showed a red emission. In order to increase the probability of recombination of electron and hole, a hole-transport (electron-blocking) layer or an electron-

## Keywords

Aluminum complex, Organic light-emitting diode, blue-green emission

transport (hole-blocking) layer is usually inserted in the devices.

In layered organic LEDs, there is a possibility that exciplex formation takes place at the interface between the charge-transport layer and the emitting layer for certain combinations of emitting and charge-transport materials, affecting the emission color. Exciplex formation at the organic solid interface is a subject of interest; however, there have been few reports which describe in detail the exciplex formation at the organic solid-state interface in organic LEDs [5-8].

In this paper, we report bilayer devices with PVK as the hole transport layer and an aluminum complex (Al(DBM)<sub>3</sub>) as the emitting layer. Absorption, photoluminescence (PL) and electroluminescence (EL) results demonstrate that the emission was due to exciplex formation at the interface between the PVK and Al(DBM)<sub>3</sub>. The PL of the mixture of PVK and Al(DBM)<sub>3</sub> and EL of bilayer films are dramatically different from that of the single layer films of PVK and Al(DBM)<sub>3</sub>.

## 2. Experimental details

### 2.1 Measurements

The EL and PL spectra were measured with a SPEX-FL-2T2 spectrofluorimeter. The luminance was measured with a calibrated ST-900 luminance meter. The power supply that increased the applied voltage at a rate of 1 V/4s was controlled. All measurements were carried

out at room temperature in ambient atmosphere.

## 2.2 Preparation of the sample

Al (DBM)<sub>3</sub> was synthesized as follows: An alcoholic solution of Aluminum chloride was added to an alcoholic solution of dibenzoylmethane by stirring with a molar ratio of the dibenzoylmethane to Al<sup>3+</sup> of 3:1. The pH value of the mixture was adjusted to 6-7 by adding an aqueous solution of sodium hydroxide. The precipitate was filtered, washed with water and ethanol, dried at 60 °C, and then stored in a silica-gel desiccator. Analysis (%C<sub>45</sub>H<sub>33</sub>O<sub>6</sub>Al), Found (calculated): C, 77.23 (77.50); H, 4.81 (4.74); O, 14.23 (13.78); Al, 3.84 (3.88).

## 2.3 Preparation of EL devices

The device structures are shown in Fig.1. Al (DBM)<sub>3</sub> was used as the emission center. The devices were prepared on a glass substrate coated with a patterned indium-tin-oxide (ITO) with a sheet resistance of 70 Ω/m<sup>2</sup>. The hole-transporting layer PVK, having a molecular weight of 150000 purchased from Kanto Chemical Ltd., was spin coated onto ITO using chloroform as the solvent, and the thickness of the PVK layer was about 100 nm. Al (DBM)<sub>3</sub> was deposited by vacuum evaporation at a pressure below 3×10<sup>-3</sup> Pa. The deposition rates were maintained to be 2 Å/s. Then a 1500 Å-thick Al was deposited on the organic layer surface as the top electrode at the same vacuum pressure, the deposition rate was maintained to be 10 Å/s. The area of EL devices was 2×2 mm<sup>2</sup>.

## 3. Results and discussions

Several devices were prepared in order to establish the thin film properties of Al (DBM)<sub>3</sub> (Fig. 1). Single and double layer structure without a hole transporting layer (Fig. 1, a, b) failed to produce EL. This indicates that the Al (DBM)<sub>3</sub> compound does not have the hole transporting capability. Perhaps the Al (DBM)<sub>3</sub> has high ionization potential (c.f. 4.8eV for tris

(8-hydroxyquinolino) aluminum (Alq<sub>3</sub>)). The introduction of a 100 nm thickness HTL (PVK) into a single layer device (Fig. 1.c) resulted in EL with broad components in the blue and green region of the visible spectrum. Fig. 2 shows the EL spectra for the device using Al (DBM)<sub>3</sub> as the emitting material and PVK as the hole transport material. The EL spectra were different from the PL spectra of PVK and Al (DBM)<sub>3</sub>, shifting to a longer-wavelength region. This observation indicates that Al(DBM)<sub>3</sub> acts in the device as both an emitting layer and an efficient ETL. It is suggested that exciplex formation takes place at the organic solid-state interface between Al (DBM)<sub>3</sub> and the hole-transport material, PVK, resulting in blue-green emission. The exciplex formation was evidenced by the measurement of the PL spectrum of spin-coated film of the equimolar mixture of Al (DBM)<sub>3</sub> and PVK. The film was spin-coated at 2800 rpm from a 10 mg/ml chloroform solution onto quartz substrate. Fig. 3 shows the PL spectra of the spin-coated solid films of PVK, Al (DBM)<sub>3</sub> and their mixture. The PL of single PVK layer excited at 370 nm has an emission peak at 420 nm, similar to previous reports of the PL of PVK [9,10]. The PL for single layer Al (DBM)<sub>3</sub> film excited at 296 nm shows an emission peak at 412 nm. When excited at energy equivalent to the excitation energy for the single PVK layer (λ<sub>max</sub> = 420 nm) and Al (DBM)<sub>3</sub> layer (λ<sub>max</sub> = 412 nm), the mixture shows a new emission peak at 476.8 nm, which we identify with an exciplex. The EL spectra for the devices were found to be in good agreement with the PL spectra of the equimolar mixture of Al (DBM)<sub>3</sub> and the hole-transport material, PVK. The exciplex formation between Al (DBM)<sub>3</sub> and PVK was further confirmed by the measurement of the fluorescence lifetimes of the spin-coated solid films of PVK, Al (DBM)<sub>3</sub> and their equimolar mixture. Whereas the time-

resolved photoluminescence decay curves of the spin-coated film of Al (DBM)<sub>3</sub> alone were analyzed by a single-exponential decay, that of the film of an equimolar mixture of Al (DBM)<sub>3</sub> and PVK was analyzed to be involving two components. Table 1 lists the photoluminescence lifetimes of the films of the equimolar mixture of Al (DBM)<sub>3</sub> and PVK together with those of the solid films of Al (DBM)<sub>3</sub> and PVK alone. The fluorescence of the mixture of Al (DBM)<sub>3</sub> and PVK involves components of much shorter lifetime than those of Al (DBM)<sub>3</sub> and PVK alone, which are attributed to the exciplexes. It should be noted that the emission color can be tuned by varying the applied voltage. With an increase in the applied voltage, the emission color tended to become green and the EL spectra underwent red shift as shown in Fig. 2. Fig. 4 shows the current density-voltage and EL intensity-voltage characteristics of the double-layer LED. When the LED was forward biased with the ITO electrode at positive polarity, blue-green EL was observed. However, when the device was reverse biased, EL was not observed implying that is not introduced by the dielectric breakthrough of the layer system. The brightness of the device was about 45.6 cd/m<sup>2</sup> at a dc driving voltage of 15 V and current density of 480 mA/cm<sup>2</sup>, and an EL efficiency of 0.55 lm/w at a drive voltage of 12 V and current density of 106 mA/cm<sup>2</sup> was found. In summary, heterojunction of PVK and Al (DBM)<sub>3</sub> show a strong photoluminescence and electroluminescence feature due to exciplex emission at the interface. The exciplex was evidenced by the measurement of PL spectra and lifetimes. The emission color can be tuned by varying the magnitude of applied voltage.

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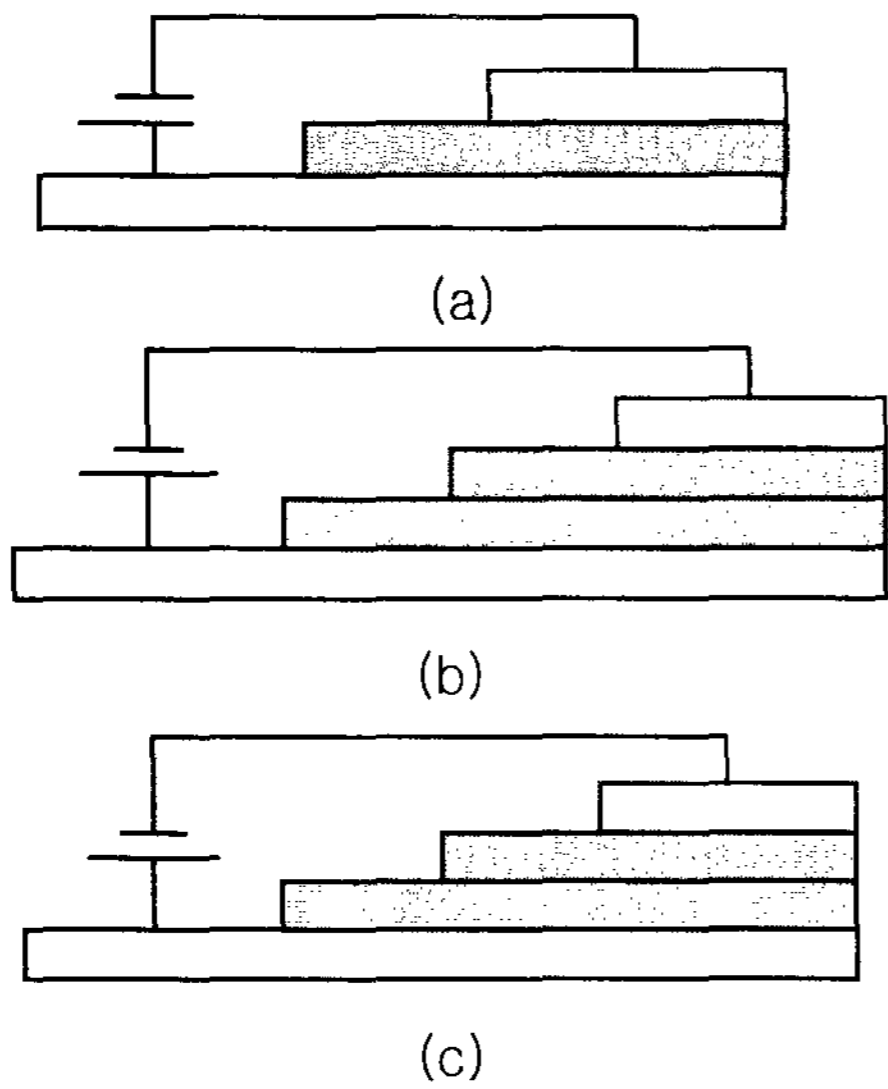


Figure 1. Configuration of the Al(DBM)<sub>3</sub> EL cell

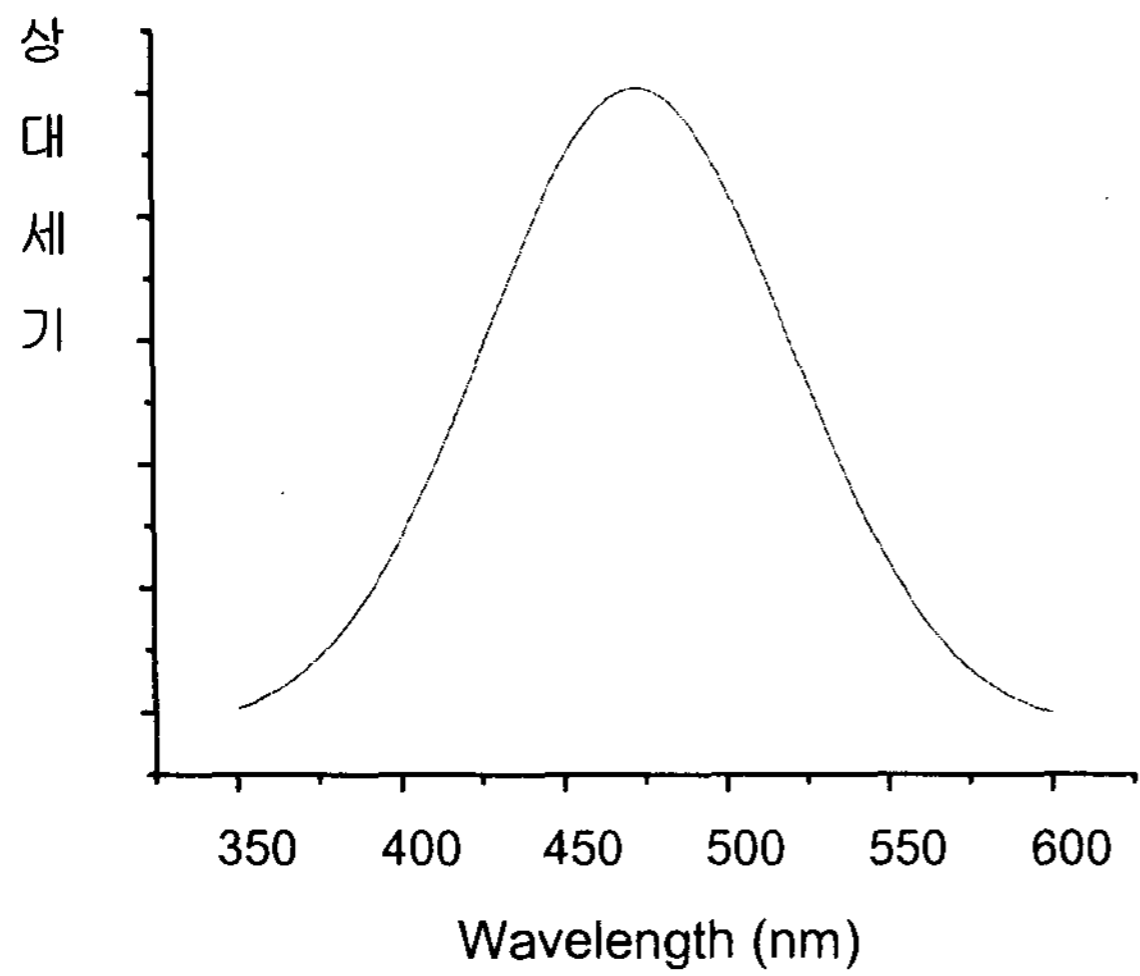


Figure 2. The electroluminescence spectrum of Al(DBM)<sub>3</sub> thin film

Material	$\tau_1$ (ns)	$\tau_2$ (ns)
Al(DBM) <sub>3</sub>	37	
PVK	18	42
Al(DBM) <sub>3</sub> :PVK	8.3	51

Table 1. Fluorescence lifetimes of Al(DBM)<sub>3</sub>, PVK and an equimolar mixture of Al(DBM)<sub>3</sub> and PVK in solid thin films.

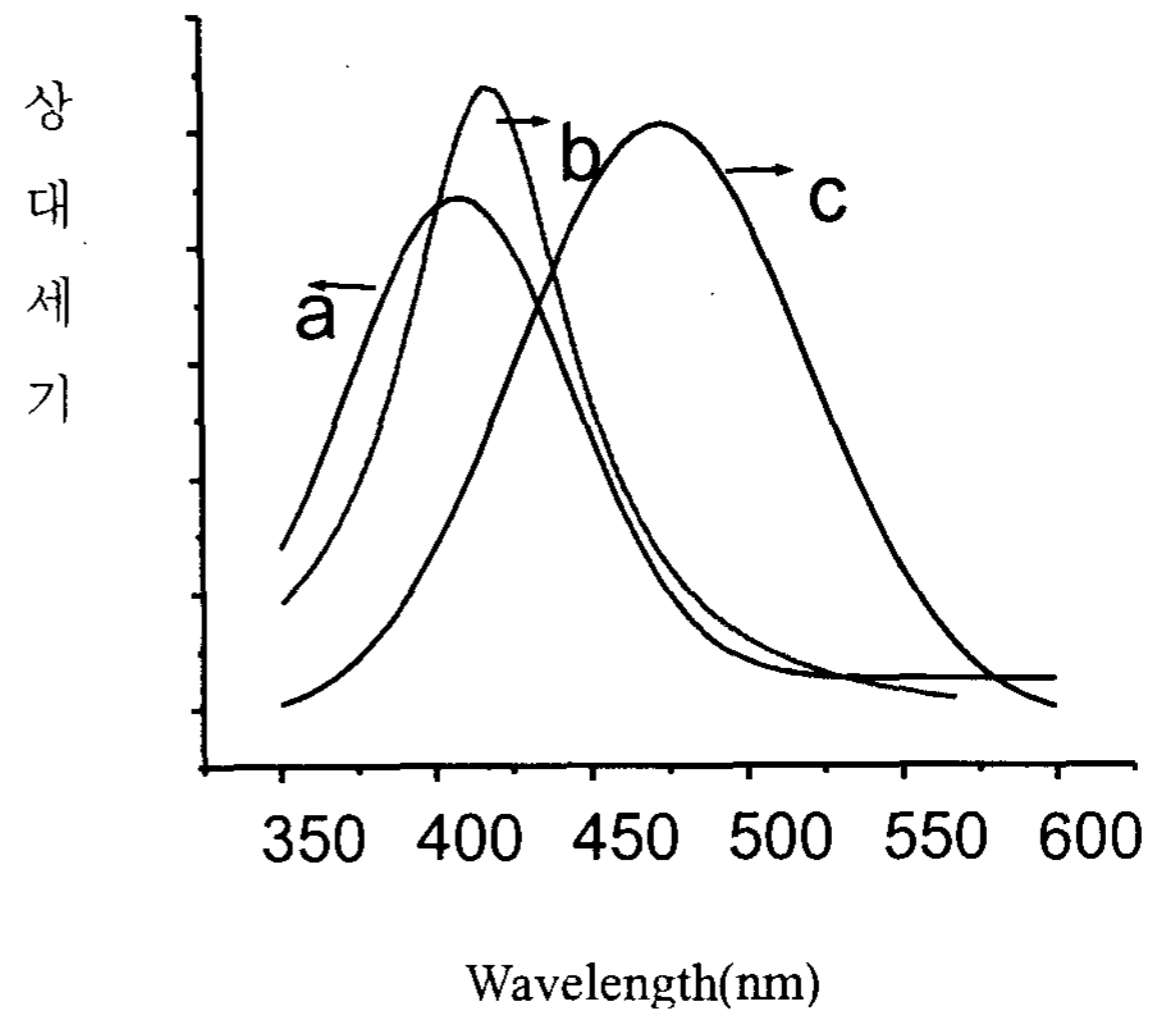


Figure 3. The photoluminescence spectra of the spin-coated solid films of PVK(a), Al(DBM)<sub>3</sub> (b) and their mixture(c)

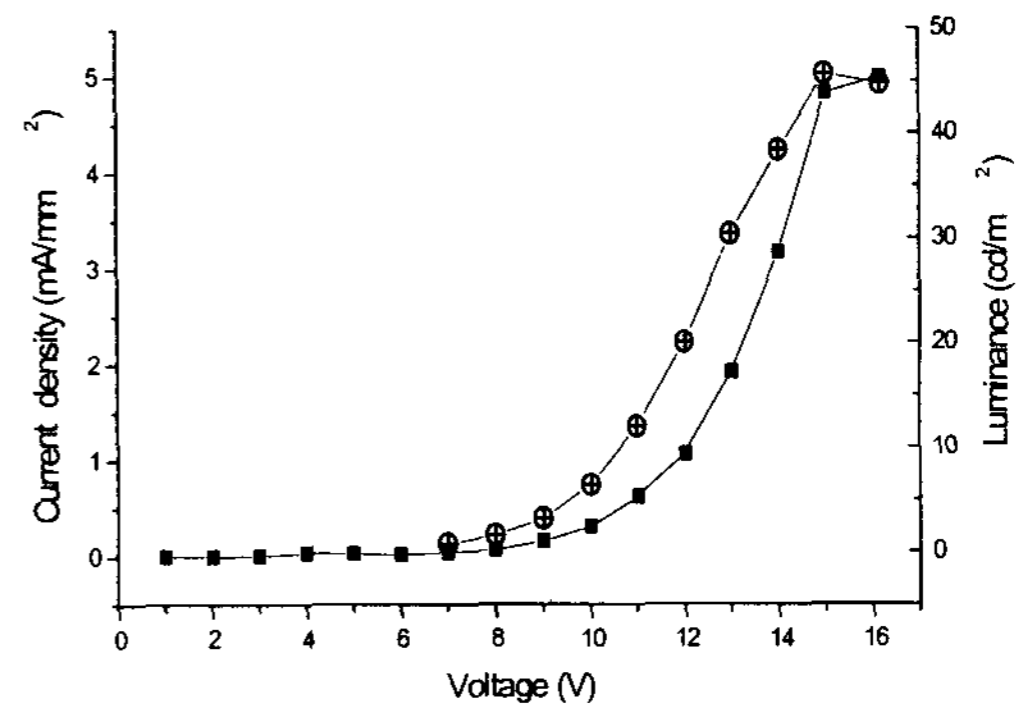


Figure 4. Current-Voltage (■) and Luminance-Voltage (⊕) characteristics of a typical bilayer light-emitting device.