Elucidation of the Aggregate Formation in the Organic Light Emitting Diode

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Abstract : The color stability and purity from OLED is of current interest. Aggregation of dyes alters the device color after fabrication of the devices. Exciplex and electroplex formations have been proposed to explain the aggregate color change. We investigate the possibility of exciplex formation and propose the new electroplex state that can cause the bathochromic shift of the electroluminescence spectrum from the devices with TPD/PBD layers. The photoluminescence maximum of the device was 420nm, and the electroluminescence maximum of the device to became 480nm. The bathochromic shift cannot be attained with photoluminescence study with highly concentrated TPD/PBD mixture. This clearly indicates that the 480nm spectrum of the devices is not resulted from the exciplex formation with TPD and PBD. We observed the overshoot in EL spectrum from the OLEDs. The most intense overshoot was observed at 460nm, which may be due to the aggregates that are formed after the electric field has been removed from the devices.

Keywords : aggregation, OLED, overshoot, exciplex, electroplex.

1. INTRODUCTION

Elongation of lifetime and improvement of color characteristics for the development of electroluminescent devices draw a lot of attention recently[1,3]. The oxidation of dyes and electrodes, the physical damage at the interfaces under a high electric field, and the aggregation of dyes are the major issues in these days[4,6]. The aggregation of dyes for the blue emission devices shifts the color to greenish blue, which does not produce clear blue color from the display devices.

The solid-state luminescence devices always tend to emit red shifted light, especially far blue emission due to the formation of the dye aggregates[7]. The formation of aggregates changes the emission spectrum and emission efficiency. The exciplex is the complex and the aggregate, which formed with an excited molecule and a non-identical molecule. A number of papers claimed that the red-shifted emission was from the exciplex formed at the interfacial region between the organic layers. Sasabe showed the difference in spectrum between single layer device and the double layer device, which emitted red shifted light at the

interfacial region of polycarbazole film[2]. Similar result was obtained from the devices with the triphenyldiamine and quinoxaline, and the device with polyvinylcarbazole (PVK) and polyphenylene derivative[2,8]. A couple of results compared the exciplex emission from the mixture of the dyes and electroluminescence, but only showed the possibility of the exciplex formation during electroluminescence process[9,10].

The electroplex is the complex that was formed with two non-identical molecules at the interface between two organic films under a high electric field.[11]   Since the films consisting of the OELD are under very high electric field, the organic materials can generate new states and provide new transitions between these states.

In this study, we investigate the possibility of exciplex formation and propose the new electroplex state that can cause the bathochromic shift of the electroluminescence spectrum.

2. EXPERIMENTAL

The molecular structures of the materials, CuPC-a (Phthalocyanine copper), TPD (N,N′ – Diphenyl – N,N′ – di(m-tolyl) – benzidine) and PBD (2 – (4-Biphenylyl) – 5(4-tert-butyl-phenyl) – 1,3,4 – oxadiazole) are shown in Fig. 1. These materials are commercially available from the Aldrich and used without further purifications.   The structures of OLEDs areas shown in Fig. 1. The indium tin oxide (ITO) covered glass (supplied by Samsung Corning. Co.)   was used as a transparent electrode. The ITO was patterned using HCl and a patterned mask. Then the ITO was cleaned with methylene chloride for 15 min in an ultrasonic bath, and then lets the ITO simmer in the mixed

solution of ultrapure water, hydrogen peroxide and liquid ammonia. Finally, ITO was rinsed from ultrapure water. After that, organic materials were evaporated on the ITO surface by the conventional thermal evaporation technique under 10^{-5} torr. The evaporation rate of the organic material was approximately 0.05-0.2 nm/s. A thin layer of LiF(0.6nm) was deposited on top of the organic layer by thermal evaporation under 5×10^{-6} torr. And 150nm of Al electrode was layered on LiF layer under the same conditions.   Every single device was encapsulated under Ar atmosphere.

For the UV/visible absorption spectra and photoluminescence spectra, a 10^{-3}-10^{-7} mol% TPD solution in chloroform, a 10^{-3}-10^{-7}mol% PBD solution in chloroform and a 10^{-3}-10^{-7} mol% TPD-PBD solution in chloroform, diluted in 1:1, were measured. The UV/visible absorption spectra were obtained using an HP8452A   spectrophotometer.   The photoluminescence spectra of the solutions and solid films were obtained using Perkin Elmer LS50B. The current density-applied voltage(J-V) characteristics of the diodes were measured using a Keithley 236 SMU source-measure electrometer only with DC forward bias. For the electroluminescence spectra of the devices the emission spectra was taken with the same set-up as for the photoluminescence measurements. Fig. 2. illustrates schematically the experimental setup for the transient EL measurements. It consists of a pulse generator and a fast photo detector coupled with a suitable automated acquisition system, which is triggered by the voltage pulse generator. All the measurements were performed in atmospheric condition and at room temperature.
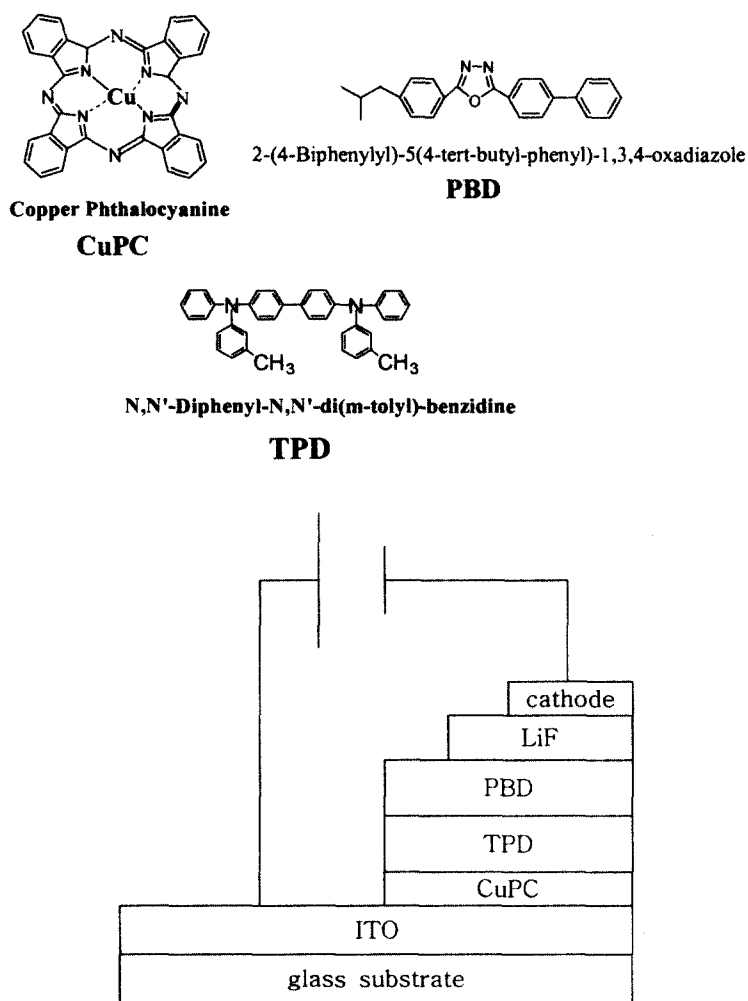
2-(4-Biphenylyl)-5(4-tert-butyl-phenyl)-1,3,4-oxadiazole

PBD

Copper Phthalocyanine

CuPC

N,N'-Diphenyl-N,N'-di(m-tolyl)-benzidine

TPD

Fig. 1. The molecular structure of materials and the schematic of the device structure.

monochromator

Si-photodiode

Pulse generator

OLED   **PMT**

Storage Oscilloscope
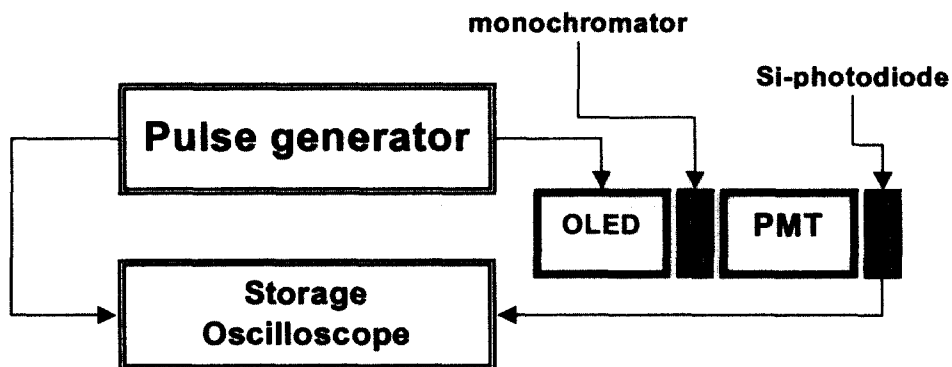
Fig. 2. Scheme for the measurements of transient EL spectrum.

3. RESULTS AND DISCUSSION

The entire device showed characteristic diode current density J vs. applied voltage V curves. The current density detected under forward bias was much higher than the current density detected under reversed bias. As can be seen in Fig. 3, the device with LiF layer shows lowest turn-on voltage. The thin LiF layer lowers injection barrier for the electrons into the organic layer from the metal electrode. The LiF layer also increases the current density of the devices under the same electric field. Many studies elucidate that the LiF layer improves the device performance[12,13]. The LiF layer not only improves the current density but it enhances the device performance such as stability and lowered turn-on voltage. In most cases, the LiF does not affect the spectral properties of the devices. The thickness of the TPD layer influences the current density of the devices. The current density was increased by one or two orders of magnitude for the thick (60nm) TPD layer for devices with LiF layer.

The photoluminescence spectra of the PBD solubilized in chloroform did not change much over the concentration range from 10^{-7} M to 10^{-3} M. This indicates that the aggregates of the PBD did not form or at least did not emit light from the excited state. However, the luminescence maximum of TPD gradually shifts from 370nm (10^{-7} M) to 420nm (10^{-3}M) as the solution becomes concentrated(Table 1).
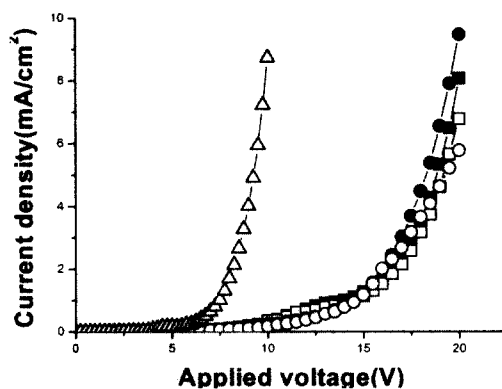

Fig. 3. Current density J vs applied voltage V of devices; ITO/CuPC-a(10nm)/TPD (50nm)/PBD(50nm)/ LiF(0.6nm)/Al (200nm)(open triangle); ITO/CuPC-a (5nm)/ TPD(50nm)/PBD(50nm)/ Al(200nm)(solid circle); ITO/CuPC-a (10nm)(solid square); ITO/CuPC-a(15nm) /TPD(50nm)/PBD(50nm) /Al(200nm)(open square); ITO/TPD (40nm)/PBD(60nm)/Al(200nm) (open circle).

The lowest energy transition maximum observed for TPD was at 425 nm and the fluorescence tail traces back to 480nm. The mixture of TPD and PBD film casted onto the quartz plate did not produce aggregate emission peak other than the emission peak of TPD and PBD themselves. This indicates that the TPD and PBD do not generate the TPD-PBD exciplex with irradiation of UV-light.

Table 1. PL Characteristics of TPD in Organic Solvent Dependent on Concentration of TPD

Concentration of TPD in CHCl₃[mole/L]	Emission Max. at [nm]	Take-off at [nm]	Band width [nm]	Full width half maximum(FWHM)[nm]
10^{-7}	370	320	170	58
10^{-5}	396	323	173	70
10^{-4}	410	379	121	40
10^{-3}	420	381	119	43

The devices with TPD and PBD films and without CuPC layer exhibit two electroluminescence peaks at 410nm and 470nm(Fig. 4). The longer wavelength peak was the peak that could not be observed from the photoluminescence spectra. The bathochromic shift of luminescence spectra from the photoluminescence maximum has been observed from other dyes and systems[14]. The bathochromic phenomena are detrimental for the realization of pure blue emission from the devices.

The relative intensity of the peaks is variable with the configuration of the devices. The intensity of the 470nm peak is higher for the devices using CuPc-aand LiF(see Fig. 4). Short wavelength emission was strong from the devices under high electric field compared to those under the low electric field. The field effect on the electroluminescence spectra may be due either to the newly generated states under high electric field or to the dynamics of the electrons and states as a function of the electric field strength. The 410 nm band is the transition from the excited state that is the same as photo-excited state. The 470nm band is produced from the newly generated state under electric field. The dynamics between these two states under electric field can alter the emission spectrum of the devices. The mechanism and dynamics of the electroluminescence behavior has to be understood before discussing the spectral shift from the electroluminescence devices.

The aggregation of dye molecules is very common when the concentration of dye molecules is high. The molecules at excited stated tend to form eximer or exciplex which exhibit either hypso- or batho-chromic shift in emission spectrum. To understand photophysics of the bathochromic shift in electroluminescence spectrum, the photoluminescence of the PBD and TPD at various concentration and solid film on the quartz slide was examined(see Fig. 5 and
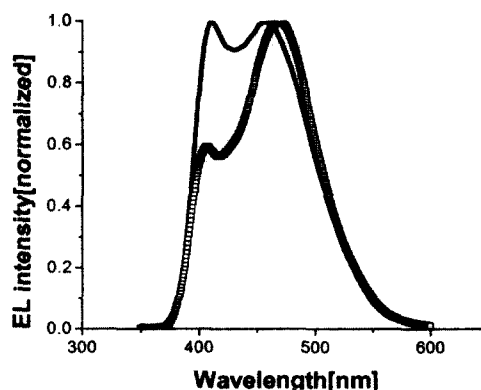
Table 1).

Fig. 4. Electroluminescence spectra of devices : ITO/TPD/PBD/Al(solid line); ITO/CuPC/TPD/PBD/LiF /Al(square line).

The concentration range of the PBD and TPD solubilized in chloroform was $10^{-7}M$ to $10^{-3}M$. Over the concentration range, the fluorescence spectrum of PBD did not change much, and was slightly shifted to the red when the concentration of the solution was $10^{-3}M$. Photoluminescence peak of TPD was shifted from 390nm to 425nm as the concentration of the TPD became high. The dramatic shift was also observed from the mixture of TPD and PBD solutions(see Fig. 6). This shift was due to the Foster energy transfer from PBD to TPD at high concentration[15].

Sasabe explains that the 30nm batho-chromic shift of polycarbazoles emission from the electroluminescence devices is due to the formation of exciplex[2]. There are quite a few examples tried to justify that the batho-chromic shift in electroluminescence spectrum was resulted from the excimer or exciplex formation[16]. It was claimed that the exciplex formation because the red shifted electroluminescence spectrum was observed from the bi-layer devices and single layer devices did not exhibit any of these. Wu et.

al. identified the exciplex formation by photoluminescence experiment with the 1:1 mixture of DPA and Bph$_2$q and observed the similar emission spectrum from electroluminescence devices[17].
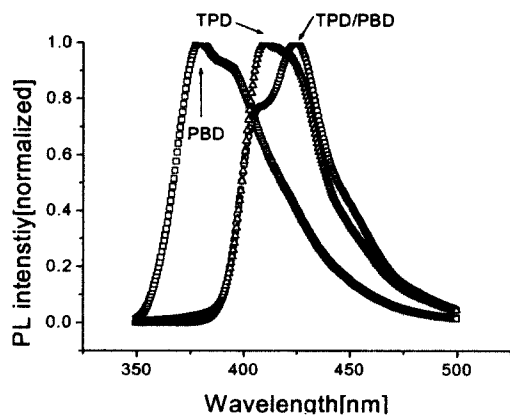

Fig. 5. PL spectra of solid films on quartz plate of PBD, TPD, PBD/TPD (TPD/PBD=1 in molar ratio).
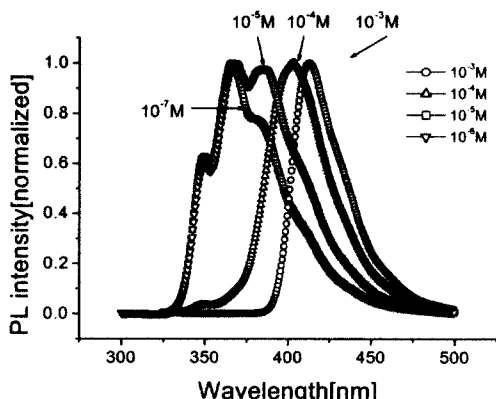

Fig. 6. PL spectra of TPD/PBD mixture in CHCl$_3$ (TPD/PBD=1 in molar ratio) dependent on concentration.

The onset of the EL that corresponds to t_d can be considered as a maximum for the transit time of either the fastest or the slowest charge carriers. And the saturation time of the EL(t_r) which can be considered

as the time the electrons need to reach the anode[18]. This would lead to the electron mobility on the order of 10^{-6} cm^2/Vs. From t_d = 0.5 ~ 1 m sec, the mobility of electrons or holes can be on the order of 10^{-6} cm^2/Vs. This clearly indicates that the mobility estimated from t_d is that of electrons, not holes. The hole mobility of TPD is on the order of 10^{-4} and 10^{-3} cm^2/Vs, which is obtained by TOF measurements[19]. The values are much larger than the mobility values calculated on the basis of the t_d(see Table 2).

Rommens et. al. got the hole mobility from t_d. The mobility values are on the order of 10^{-6} cm^2/Vs in our case[20]. This value is too small for the hole mobility of TPD layer.[19] Although Redecker and co-workers suggested that the hole mobility in an organic LED is up to one order of magnitude larger than the mobility calculated from the transient experiment, the hole mobility of our case is one or two orders smaller than the literature value[18,19]. Redecker indicated that the t_d corresponded to the time that the electrons needed to migrate through the ETL. The onset time is the time that the electrons to reach the interface with HTL. The electron mobility of 10^{-7} cm^2/Vs at 1.2 × 10^{6}V/cm was obtained from double layer OLEDs using PBD-doped layer as ETL[21]. This value is one order smaller than that of our results. This can be understandable for the devices with doped with PBD compared to the devices with pure PBD layer.

t_r and t_d are field dependent. According to the theory of Redecker and co-workers, the mobility obtained from t_r is the weighted average of the electron mobilities in both layers and the time necessary for an electron to go from the ETL to the HTL. Therefore both transit times are dependent on the electric field applied across the organic layer.

Table 2. Hole and Electron Mobilities(cm^2/Vs) Calculated from the Results of Transient EL Measurements and Using the Equation m=d/tF at Applied Voltage 14V, where m is Mobility of Hole and Electron, d is Thickness of Organic Layer, t is Measured Time and F is Electric Field. For Hole Mobilities the Value of d is the Thickness of TPD and t is t_d and for Electron Mobilities the Value of d is the Thickness of Whole Organic Layer and t is t_r. F is the Electric Field at 14V.

Emission site(nm)	410	420	430	440	450	460
μ_h from t_d	9.4×10^{-6}	4.6×10^{-6}	9.4×10^{-6}	4.7×10^{-6}	4.7×10^{-6}	9.7×10^{-6}
μ_e from t_d	7.9×10^{-6}	3.9×10^{-6}	7.9×10^{-6}	3.9×10^{-6}	3.9×10^{-6}	7.9×10^{-7}
μ_e from t_r	1.2×10^{-6}	1.7×10^{-7}	1.4×10^{-6}	1.4×10^{-6}	1.6×10^{-6}	1.7×10^{-6}

The overshoot in EL spectrum has been observed from both single and double layer OLEDs[22,23]. The overshoot is the abrupt increase in emission intensity after turn-off the electric pulse. The devices that showed the overshoot contained dye-dispersed polymer films and had electron mobility of the polymer films about 10^{-7} cm^2/Vs. Rommens and co-workers have reported a dual electroluminescence of OLEDs and the EL overshoot with PBD-dispersed polymer layer as ETL[20]. They showed that the relative intensity of the EL overshoot of double layer type OLEDs was much more intense than that of the mono-layer type OLEDs. We could not observe the dependence of the pulse duration on the overshoot intensity. The intensity of the overshoot was wavelength dependent. The most intense overshoot was observed at 460nm(see Fig. 7 and 8). The intensity was more than 3 times stronger than that observed at other wavelengths. The high intensity in double layer system may be due to the accumulation of charge after the electric field has been removed. The diffused charge can generate the new local electric field at the interfacial region. The accumulated charge at the interfacial region can produce electroplex,

which can be very distinct dimer structure like J aggregate. J aggregates generally exhibit very sharp bathochromic emission spectrum. In our case, the sharp 460 nm emission may be due to the aggregates, which are formed after the electric field has been removed from the devices. The large intensity is due to the dipole allowed transition of J-aggregates and space charge induced easy formation of aggregates at the interfacial region.
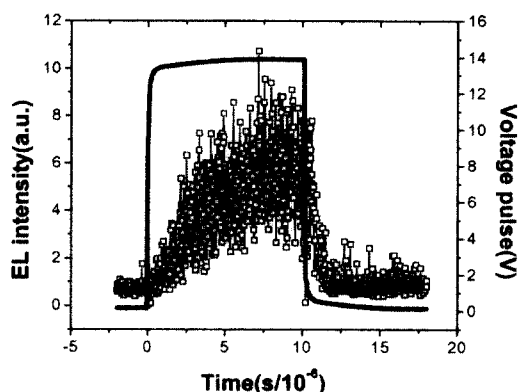

Fig. 7. Transient EL spectrum from OLED(ITO/CuPC-a(10nm)/TPD(50nm)/ P B D (5 0 n m) / L i F (0 . 6 n m) /Al(200nm)) emission at 410nm.
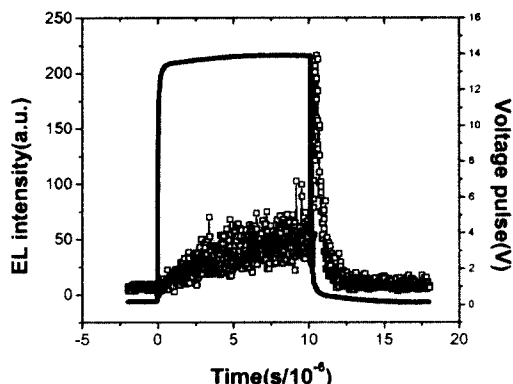
Fig. 8. Transient EL spectrum from OLED (ITO/CuPC-a(10nm)/TPD(50nm) /PBD (50nm) /LiF(0.6nm) /Al(200nm)) emission at 460nm.

4. CONCLUSIONS

In this article, we reported on the bathochromic shift in EL spectra of OLEDs of bi-layer systems. A newly appeared emission peak in longer wavelength region could be attributed to the formation of new excited state of electron-hole pair like as exiplex. We could not observe such red-shift in even concentrated solution PL spectra of TPD, PBD and mixture of TPD-PBD solution. From the transient EL spectra we could estimate the electron mobility which was lower one order than that from literatures. Since the overshoot effect in transient EL spectra could be an evidence the accumultion of carriers(holes) at the interface of organic layers in OLEDs, the bathochromic shift in EL spectra could be attributed to the accumulation of carriers(hoels) at the interface of organic layers.

ACKNOWLEDGEMENT

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