Device performance and carrier dynamics in blue mixing host organic light-emitting devices

Jiun-Haw Lee*[a], S. W Liu[b], Chih-Chung Teng[a], Jian-Hong Lin[a], Tian-Chiun Lin[a] and C. C. Yang[a]
[a]Graduate Institute of Graduate Institute of Electro-Optical Engineering and Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C.;
[b]Institute of Chemistry, Academia Sinica, Taipei, Taiwan, R.O.C.

ABSTRACT

In this paper, we study device performance and carrier dynamics of an organic light-emitting device (OLED) with an emitting layer (EML) based on a mixed-host (MH) structure. Such a structure is composed of two different host and one dopant materials. It exhibits longer operation lifetime as compared with a conventional heterojunction (HJ) device. In such a MH layer structure, carrier transport characteristic is modified and emission zone position is changed. Energy transfer from the two hosts to one dopant is studied by EL, PL and TRPL measurements. We observe spectrum shift from the EL measurement under different current injection. Incompletely energy transfer from NPB to DPAVBi is shown in cw PL measurement. Time constant at different probe wavelengths with different mixing concentration suggests that different energy transfer in such a MH structure.

Keywords: Energy transfer, host-guest system, mixing host.

1. INTRODUCTION

Recently, there has been much interest in electronically functional organic materials with respect to various applications as organic light-emitting device (OLED), spectral sensitization, and organic solar cell. Organic light-emitting device has attracted much attention because it exhibits the advantages of low-power consumption, high brightness, high contrast, and low cost [1],[2]. In such a device, doping high internal quantum efficiency (IQE) material inside the charge transport material to form an emitting layer (EML) can effectively increase the spectral region of the emission, increase device lifetime, and reduce unwanted self-absorption. However, in the host-dopant material system, Förster energy transfer dominates the process. This physical mechanism involves long-rang dipole-dipole coupling and results in the transfer of the excited-state energy from a host donor to a guest acceptor. Singlet exciton transfer from the host by Förster transfer and the energy level of singlet in host has to lie above the corresponding level in guest. Moreover, efficient transfer requires an overlap of emission in the host and absorption in the guest. [3],[4],[5].

The mixing host (MH) structure with the hole-transport layer (HTL) and the electron transport layer (ETL) exhibits the bipolar transport characteristics. The blurred interface between the HTL/EML and EML/ETL increases lifetime because delocalization of the recombination zone lowers the electric field at the otherwise abrupt heterojunction [6]. In the mixing host system, the long-range Förster coupling as one of the major mechanisms responsible for energy transfer following photoexcitation in the blend. Upon excitation of two hosts, the charge carriers are trapped on the dopant material where they eventually recombine [7].

Two hosts materials we used are N,N -Bis(naphthalen-1-yl)-N,N -bis(phenyl) benzidine (NPB) and (9,10-bis(29-naphthyl)73anthracene) BNA. 4,4'-bis[2-(4-(N,N-diphenylamino)phenyl)vinyl]biphenyl (DPAVBi) is used as the greenish blue emitting guest material. NPB is a hole transporting material and BNA is a host material of blue device which has deep blue emission. Adding NPB into the emissive layer delocalizes electron-hole recombination, which lowers the recombination efficiency. Although the recombination zone is delocalized, light emission is still confined by the doped region. We will focus on the energy transfer from the two hosts to the dopant guest by changing the host ratio of NPB and BNA, and observe the situation of carrier recombination.

*jhlee@cc.ee.ntu.edu.tw; phone 886 2 2363-5251 ext. 540; fax 886 2 2367-7467

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2. EXPERIMENTS

The device consisted of NPB as the HTL material with the thickness of 40nm. MH structure with 45nm that was composed of NPB and BNA with the different mole ratio, e.g. 1:0, 1:1, 1:3 and 0:1, which were labeled as A, B, C and D, respectively. EML were doped with organic fluorescent dyes DPAVBi with 2% concentrations. The ETL material used is bis (10-hydrox-ybenzo[h]quinolinato) beryllium (Bebq$_2$) as the, and finally a LiF/Al alloy as the cathode in the Fig. 1.

Photoluminescence (PL) measurement was carried out at room temperature with a 325-nm line He-Cd laser to obtain the relative quantum efficiency, full width at half maximum (FWHM) and the peak wavelength of different samples. The time-resolved photoluminescence was performed by using a Hamamatsu streak camera (Hamamatsu Photonics KK, Japan) in conjunction with a 25-cm monochromator using a 600 lines/mm grating. The excitation pump beam of λ_{exc}= 356 nm was from the second-harmonic generation of a mode-locked Ti:sapphire laser with a pulse width of 100 femtosecond and a repetition period of 13.16 ns.

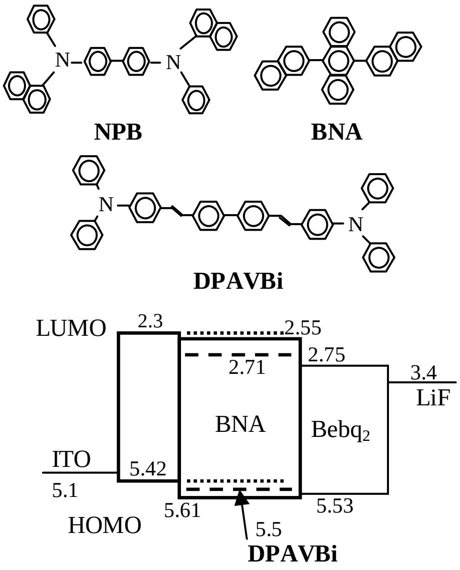


Fig. 1. Molecular structures of materials and band structure of a device.

3. RESULTS AND DISCUSSIONS

Photoluminescence spectrums of materials are shown in the Fig. 2. Peak positions of NPB, BNA, and Bebq$_2$ were 421, 447 and 494.5nm. The guest dopant material, DPAVBi, has two emitting peaks at 465 and 486nm. Fig. 3(a) shows the EL spectrum at 10 mA/cm^2. We can see that peaks of sample A and B were 505 and 498.5nm that comes from the emission from the Bebq$_2$. Since NPB is a HTL material, it causes the hole passes through the EML and recombine with electrons in the ETL when NPB concentration in EML is high. In our device structures, there were no hole-blocking layer (HBL) to obstruct hole injection at ETL. When the mixing ratio of NPB to BNA is over 1:1, the electron-hole recombination region shifts to the interface between EML and ETL. When the mixing host concentration of BNA increases, the recombination process takes place in EML rather than ETL. We can see that in Fig. 3(a) the emission of sample C and D is mainly from the DPAVBi. However, devices with mixing layer exhibits lower current efficiency due to worse energy transfer.

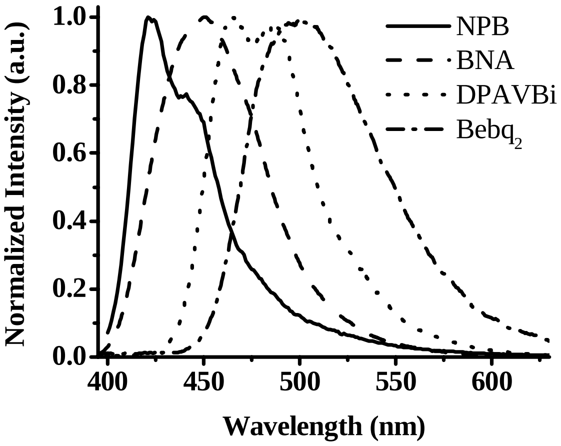
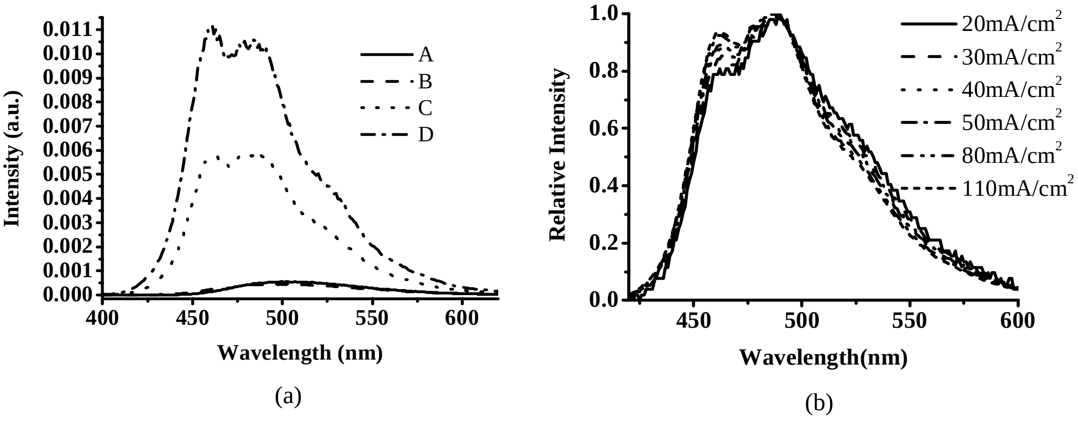


Fig. 2. PL spectrum of single film.

In sample C, the CIE coordinates of EL will blue-shift from (x=0.16, y=0.35) to (x=0.15, y=0.26) with increasing the injection current density from 20 to 160mA/cm^2. The relative intensity of short wavelength part, i.e. 462nm, increases with increasing the current density as shown in the Fig. 3 (b). In sample C, EML was composed of 25% NPB and 75% BNA. Since the energy transfer from NPB to DPAVBi is not efficient, the mixture of NPB in EML effectively “dilutes” the host material, BNA. In the MH EML, injected carriers transport through the mixture of BNA and NPB by hopping process. Then excitons transfer their energy from host to the dopant material that emits the photons. Such a dilute host cannot supply enough excited carriers under the low injection of 20 mA/cm^2. Hence we can see that the energy transfer from BNA to DPAVBi is first from lower state, i.e. 486nm. With increasing current injection, higher state, i.e. 486nm, started to be filled up.



(a)

(b)

Fig. 3. (a) EL spectrum of different samples at 10mA/cm^2 and (b) EL spectrum of sample C with different current density.

Fig. 4 (a) and (b) shows the B-V and J-V characteristics, respectively. The luminance reaches 35090 cd/m^2 at 8.5 V, which corresponds to a luminous efficiency of 3.08 cd/A in sample D. That shows a good energy transfer from BNA to DPAVBi. The brightness is low in sample A and B, as shown in Fig. 4 (a), since the recombination process is at EML/ETL interface. The emission zone is close to the cathode and it experiences strong quenching effect from the cathode metal. In the Fig. 4(b), we can see that with increasing the HTL material ratio, operating voltage decreased due to the higher mobility of the NPB. Device C exhibits the longest operation lifetime that is six times longer than the conventional device (sample D). Those data were published in ref. 8

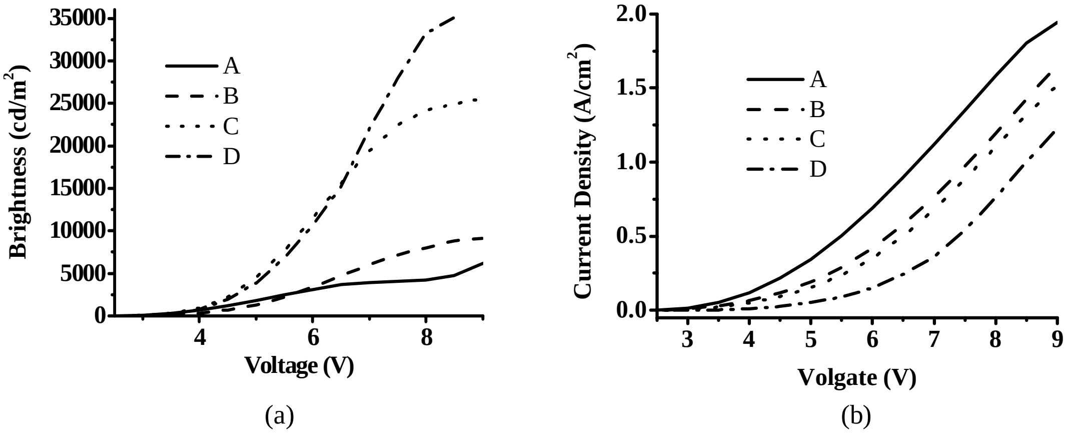


Fig. 4. (a) B-V and (b) J-V curves of the devices

Fig. 5 shows the PL spectrum with different mixing ratios. We can see that emission is mainly from DPAVBi with the peaks at 465 and 486 nm in all samples. However, a small hump is observed around 421 nm in sample A that comes from the emission from NPB. The host material in such a device is completely NPB without BNA. That is also the evidence that the energy transfer is not complete. We can also see that the intensity at long wavelength of DPAVBi emission, 486nm, is smaller in sample A since the spectrum overlap between NPB emission and DPAVBi absorption is smaller.

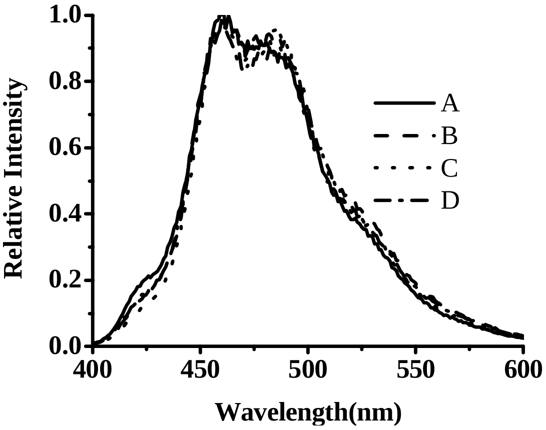
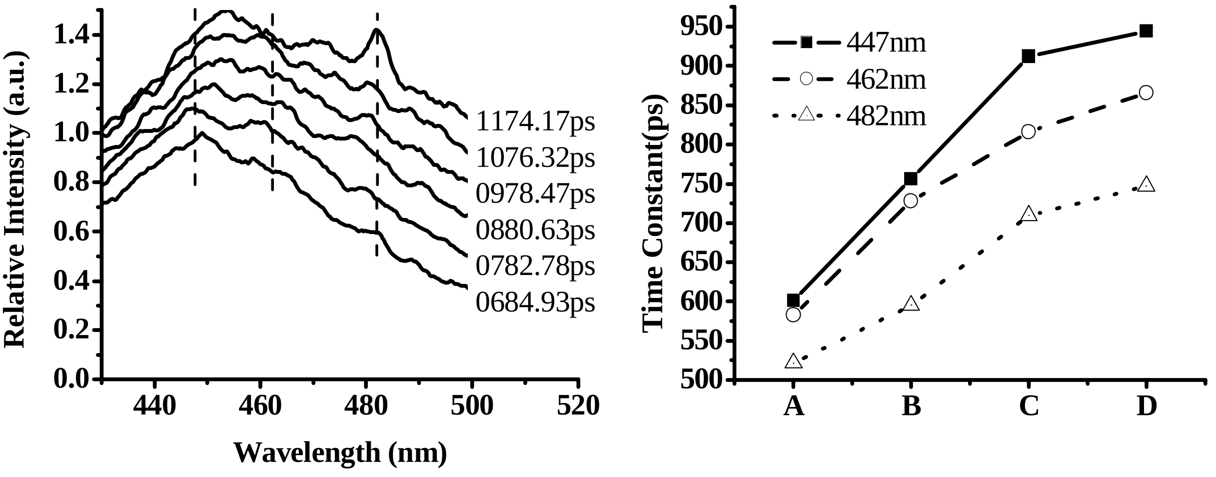


Fig. 5. PL spectrum of different devices.

In the Fig. 6(a), TRPL spectrum shows the energy transfers of the sample C from host (447nm-wavelength probed) to the two peak positions of dopant of 462nm and 482nm. Intensity of short wavelength decreases and that of longer wavelength increases. It is a typical energy transfer characteristics. We can see that the PL spectrum pumped by femto-second pulse laser is quite different from that by cw laser. Although the two peaks phenomenon cannot be observed in pulse laser case since it is not at the equivalent state, we can still probe the two wavelengths observed under the steady state excitation. We can also deduce that the decay times of 447, 462 and 482nm were 912.3, 816.3 and 709.4ps in such a sample. The long wavelength part, 482 nm, of DPAVBi emission exhibits shortest decay time that means it is efficient to relax energy from this state. If the relaxation process is radiative, that means the emission from this wavelength is most efficient. That also explains the spectrum shift in Fig. 3 (b). Excited carriers fill up the long wavelength state first followed by short wavelength one. Fig. 6 (b) shows the decay times for different samples. We can see that with increasing the BNA ratio, the time constant increases. Since the energy transfer is not efficient from NPB to DPAVBi, the short time constant does not correspond to high transfer efficiency. It may result from some kind of absorption from the MH layer. With higher NPB concentration, the absorption is more obvious. And the time constant is smaller. Such an effect results in the time constant decreases for different wavelength from 447 to 482 nm. We attribute this to the formation of excimer of NPB and BNA since only such an excimer can exhibit the long wavelength absorption.



(a) (b)

Fig. 6. (a) Time dependent spectrum of sample C and (b) time constant of different samples with different probe wavelengths.

4. CONCLUSIONS

In summary, we have reported the EL, cw PL and TRPL results of the organic thin films that compose of NPB and BNA as the EML material doped with guest material DPAVBi. Mixing layer structure changes the transport characteristics of EML and shifts the emission zone. Energy transfer among NPB, BNA and DPAVBi are also studied. Two peaks of DPAVBi corresponds to two distinct energy level and exhibits different decay time constants. An unwanted absorption is observed with increasing NPB concentration. It may come from the excimer formation of NPB and BNA.

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