Organic Electroluminescent Devices Containing Phosphorescent Molecules in Molecularly Doped Hole Transporting Layer

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Summary: We demonstrate high-efficient simple electrophosphorescent devices comprised of tris{4-[*N*-(3-methylphenyl)anilino]phenyl}amine (m-MTDATA) dispersed in a polycarbonate (PC) matrix as a hole-transporting layer (HTL), and 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) as an electron-transporting layer (ETL). The HTL doped with a complex phosphor *fac*-tris(2-phenylpyridine)iridium, [Ir(ppy)$_3$], and/or 5,6,11,12-tetraphenyltetracene (rubrene) fluorescent dye is shown to act as an emitter. Devices containing [Ir(ppy)$_3$] as a single HTL dopant show the highest external quantum efficiency (QE) reaching 9 % (photon/electron) due to direct electron-hole recombination on phosphorescent [Ir(ppy)$_3$]. A decrease in QE of one order of magnitude at high current densities is observed in all devices. Addition of rubrene to [Ir(ppy)$_3$]-doped devices shifts the maximum QE towards larger current densities.

Keywords: charge transport; host-guest systems; luminescence; organic light-emitting diodes (LEDs); thin films

Introduction

The electron-hole recombination in organic light-emitting diodes (LEDs) results in the production of singlet- and triplet-emitting states [1]. Due to spin statistics, three times more triplets than singlets are usually created. However, in common electrofluorescent LEDs only the singlets contribute directly to the emission and triplets relaxing nonradiatively are lost for light generation. Using phosphorescent materials with radiatively active triplets provides a straight way to a significant increase in quantum efficiency (QE) of organic LEDs. Indeed, the successful application of phosphorescent molecules such as porphyrinplatinum (PtOEP) [2-5] and *fac*-tris(2-phenylpyridine)iridium, [Ir(ppy)$_3$] [4,6-11], and some other Ir(III) complexes [12-14] in

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generation of organic electroluminescence has enabled the fabrication of organic LEDs with an external QE up to 19 % ph/carrier [12]. The optimizing device performance led to the design of state-of-the art multilayer LEDs having the structure ITO/HTL/EML/HBL/ETL/Mg with four organic layers – hole-transporting layer (HTL), charge carrier combination and emission layer (EML), electron-transport/hole blocking layer (HBL) and electron-transporting layer (ETL). Typically, the EML consists of organic phosphor embedded in electron-transporting host like (CBP) [4,6-8,10,13]. So far, very few organic LEDs with simpler structures and high QE have been demonstrated [10,11,14]. Using poly(9-vinylcarbazole) (PVCz) as a host material for [Ir(ppy)$_3$] guest emitter and an oxadiazole with dimeric structure of PBD, named OXD-7, as ETL, double layer (DL) devices ITO/PVCz:Ir(ppy)$_3$/OXD-7/Mg with the maximum external QE of 7.5 % (ph/e) were fabricated [11]. In turn, the DL device comprising m-MTDATA HTL and CBP host doped with [Ir(ppy)$_3$] phosphor exhibited the peak external QE of 12 % (ph/e) [10]. In the present work we demonstrate another simple high-efficiency devices with DL structure. In our LEDs, [Ir(ppy)$_3$] dispersed in m-MTDATA-doped polycarbonate (PC) matrix form HTL and oxadiazole PBD is used as ETL. This configuration allows to obtain the external QE of 9 % (ph/carrier). We also show that the QE efficiency decrease at high current densities, commonly observed in all organic LEDs, can be partly reduced by incorporating additionally in HTL a fluorescent dye (rubrene).

Results and discussion

The molecular structures, EL device configuration and energy level diagram of the materials used in this study are shown in Fig. 1. The DL LEDs were prepared by spin-coating of HTL and vacuum evaporation of ETL. The (m-MTDATA:PC:dopant) HTL was spin-cast onto ITO (indium tin oxide) glass substrates. Then, a 100 % PBD layer (ETL) was deposited by vacuum evaporation. The sandwich devices were completed by a vacuum-deposited Ca covered with a protecting layer of Ag. The weight content of m-MTDATA in HTL was 69 – 75 %. As HTL dopants, phosphorescent [Ir(ppy)$_3$] (designated hereafter as Ir) and/or fluorescent rubrene (Rb) were incorporated. The ionization potential of m-MTDATA (5.0-5.1 eV [10,15]) makes the ITO anode a good hole-injecting contact to the HTL. In turn, the electron affinity of PBD (2.6 eV [16]) enables the Ca cathode to be an efficient injector of electrons to the ETL. From the HOMO and LUMO positions of Ir (5.4 eV and 3.0 eV [10,17], respectively) and Rb (5.4 eV and

3.2 eV [15]) it is apparent that the molecules of Ir and Rb in the (m-MTDATA:PC) matrix form effective electron-trapping sites. The method of external EL QE measurement and other experimental details are described elsewhere [17,18].

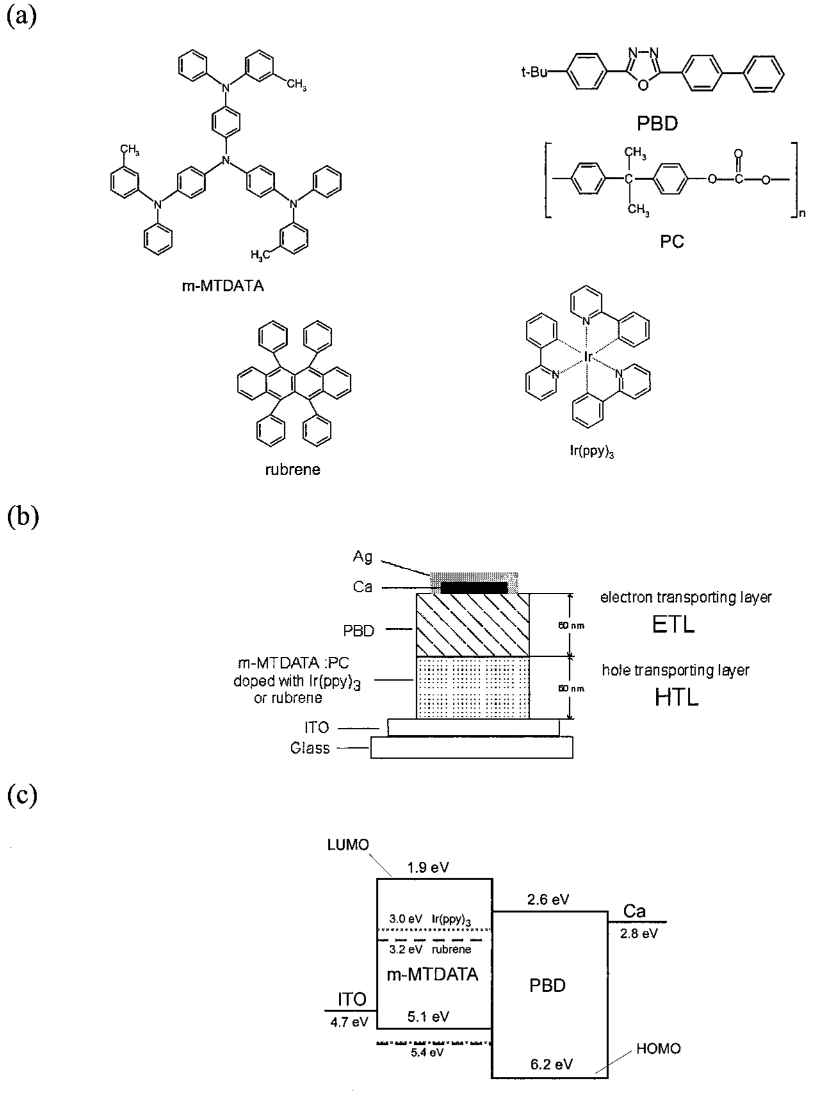

Figure 1. The molecular structures (a), EL device configuration (b) and energy-level diagram (c) of the materials used in this study

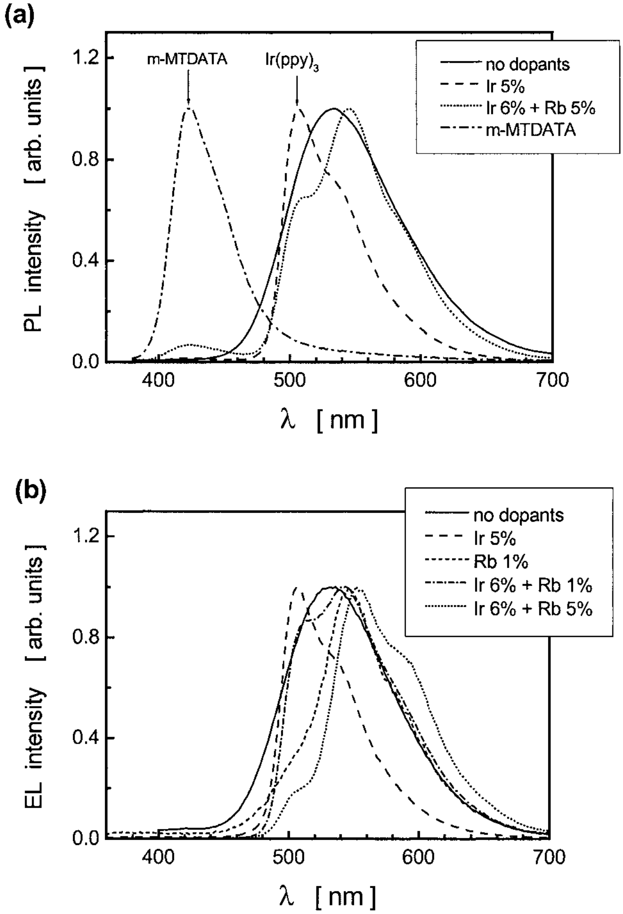

Figure 2. Normalized PL and EL spectra of devices with different HTLs: [Ir(ppy)$_3$] (Ir) and rubrene (Rb) in (m-MTDADA:PC)

Figure 2 shows the PL and EL spectra of the DL structures from Fig. 1. The spectra of undoped devices [18] are shown for comparison. The emission spectra of all devices are characteristic of the dopants (either phosphorescence of Ir or fluorescence of Rb) when doped separately, and their combination if both dispersed in the HTL. The devices exhibit the EL external QE between 0.1 % (ph/carrier) up to 9 % (ph/carrier), dependent on the type and concentration of dopant and the driving current (Fig. 3). Generally, the LEDs with Rb-doped HTLs show efficient emission at higher voltages compared with Ir-doped or undoped devices. The devices containing a small

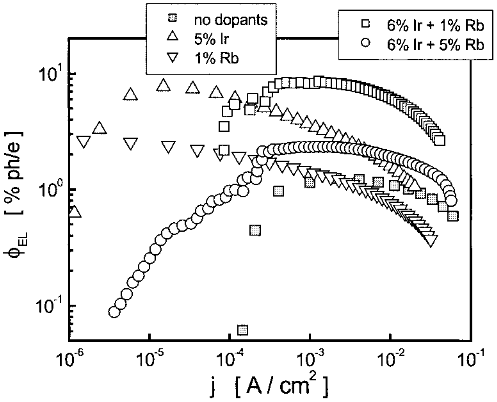

Figure 3. External quantum efficiency as a function of current density *j* for doped and undoped devices

admixture of Rb (1 %) as a single fluorescent HTL dopant show the QE values close to those of undoped devices. Since electroluminescence in dopant-free devices originates from exciplexes (m-MTDATA/PBD) [18], an efficient energy transfer from these exciplexes to Rb molecules is assumed to occur most probably in Rb-doped devices. A direct charge-trapping on Rb molecules can also contribute to this emission, similar to that for Ir-doped devices (see below). Devices containing [Ir(ppy)$_3$] as a single HTL dopant show the highest quantum efficiency (9 % ph/carrier). Considering that holes are blocked at the HTL/ETL interface and electrons are likely to be directly injected from PBD to Ir and then readily trapped on Ir molecules, direct exciton formation on Ir should be considered as a significant pathway to the efficient EL emission. Alternatively, charge recombination and exciton formation may occur first on m-MTDATA and then excitons may be subsequently transferred to Ir through the Dexter or Förster process. However, a rather high barrier for electron injection from PBD to HTL and the absence of any m-MTDATA emission in the EL spectra of undoped devices suggest that the latter process is less probable. Adding Rb to Ir-doped devices shifts the maximum QE towards larger current densities (Fig. 3). Whereas a small amount of Rb does not change the maximum value of QE, a significant decrease in QE is observed at larger concentrations of Rb. These phenomena are most probably associated with modification of electron-transporting properties of the (m-MTDATA:PC) system by Rb molecules like in rubrene-doped TPD HTL layer [19] in electrofluorescent LEDs. The common feature of all devices is a decrease in QE of nearly one order of magnitude at high current densities, independent of emission type (fluorescence or phosphorescence) of dopants. The following three mechanisms can contribute to the observed effect: exciton-exciton annihilation, exciton-charge carrier interaction and electric field-induced quenching of fluorescence or phosphorescence [4,17]. Currently we are unable to determine which process is dominant in the EL devices studied in the present work. Details of the quenching mechanism are under investigation.

Conclusions

[Ir(ppy)$_3$] and rubrene doped into HTL (m-MTDATA:PC) act as the emitters in DL devices with PBD as an ETL. Devices containing [Ir(ppy)$_3$] as a single HTL dopant show the highest QE (9% ph/carrier) due to direct electron-hole recombination on phosphorescent [Ir(ppy)$_3$] molecules. Adding rubrene to [Ir(ppy)$_3$]-doped devices shifts the maximum QE towards large current densities. The one order of magnitude decrease in QE at high current densities is observed in all devices, independent of emission type (fluorescence or phosphorescence) of dopants. Three mechanisms possibly contributing to the observed effect (exciton-exciton annihilation, electric field-induced quenching of photoluminescence, and exciton-charge carrier interaction) should be considered in further study.

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