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Comprehensive understanding of degradation mechanism of high efficiency blue organic light-emitting diodes at the interface by hole and electron transport layer

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ABSTRACT

Comprehensive study to understand the degradation mechanism of high efficiency blue organic light-emitting diodes by charge transport layers was carried out by managing the device parameters and charge transport materials. Although it has been generally accepted that the charge transport layers are important for long lifetime, the degradation mechanism was not clear. From this work, it was revealed that exciton quenching of emitters by the degradation products of charge transport layers is the main degradation pathway of blue phosphorescent and thermally activated delayed fluorescent organic light-emitting diodes. It was described that the degradation of the blue devices by the charge transport layers would be largely avoided by separating the exciton generating emitters from the charge transport layers by shifting the exciton formation zone to the center of the emitting layer. Eventually, the lifetime of the blue devices with the emission zone fall apart from the charge transport layers was not affected by the charge transport layers because exciton quenching by the degradation products of the charge transport layers was suppressed.

1. Introduction

Organic light-emitting diodes (OLEDs) are very popular as the next generation displays and are being used in a wide range of display panels like mobile phones and televisions because they have various advantages such as wide viewing angle, high contrast ratio and design versatility. However, the lifetime of OLEDs is still a challenge to expand the OLED applications [1–3]. In particular, the lifetime of blue OLEDs is a big hurdle to be overcome.

There are many mechanisms shortening the lifetime of OLEDs and the degradation factors are closely related each other [4–8]. All organic materials included in the device structure are responsible for the degradation of the OLEDs and it is being generally accepted that the emitting materials and the charge transport materials are critical to the lifetime of OLEDs [1,9–11]. It can be easily understood that the emitting materials are critical to the lifetime because the emitters are exciton generating centers [1,12]. However, the origin of device degradation by the charge transport materials was not clear although degradation of the hole transport materials (HTMs) were reported [8,13–15]. For example, the decomposition of a common 4,4'-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline) (TAPC) was reported in literature, but the degradation mechanism of the devices by the decomposition of TAPC could not be apparently explained [6,14]. The same experimental result was reported in the electron transport materials (ETMs) [16–18], but clear explanation about the degradation process of the devices was not proposed. As it is rather difficult to improve the lifetime of the devices without understanding the reason, it is highly important to elucidate the lifetime decrease by the charge transport materials. In particular, lifetime study of the blue OLEDs is required because the lifetime of the blue OLEDs is relatively shorter than that of the red and green OLEDs.

Herein, we describe the lifetime reduction of blue OLEDs by the charge transport materials in detail using a blue triplet emitter and a thermally activated delayed fluorescent (TADF) emitter. Systematic change of the charge transport materials and device structure and device analysis revealed that exciton quenching in the emitting layer by degradation products of the charge transport material is the major degradation pathway by the charge transport materials. The exciton quenching process could be controlled by isolating the excitons from the charge transport layer, which confirmed the lifetime reduction by charge transport layer induced exciton quenching.

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2. Experimental

2.1. Device fabrication and materials

The blue devices had indium tin oxide (ITO) as an anode, 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HATCN) as a hole injection layer, N_4,N_4,N_4',N_4'-tetra([1,1′-biphenyl]-4-yl)-[1,1′-biphenyl]-4,4′-diamine (BPBPA) and 4,4'-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline) (TAPC) as hole transport layers, 3,3′-di(9H-carbazol-9-yl)-1,1′-biphenyl (mCBP) as a host in emitting layer (EML), tris[1-(2,4-diisopropyldibenzo[b,d]furan-3-yl)-2-phenyl-1H-imidazole]iridium(III) ($Ir(dbi)_3$) as a blue phosphorescent dopant, (2s,3r,4r)-2,3,4,5,6-penta(9H-carbazol-9-yl)benzonitrile (5CzCN) as a TADF dopant, 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TPBI) and 3,3″,5,5″-tetra(pyridin-3-yl)-1,1':3′,1″-terphenyl (BmPyPb) as electron transport layers, LiF as an electron injection layer and Al as a cathode. The blue device structure was ITO (50 nm)/HATCN (10 nm)/BPBPA (40 nm)/PCZAC (10 nm)/emitting layer (30 nm)/TPBI (25 nm)/LiF (1.5 nm)/Al (200 nm). The emitting layer of the devices was either mCBP host doped with a phosphorescent emitter ($Ir(dbi)_3$) or TADF dopant (5CzCN) at a doping concentration of 5%. An optimized emitting layer structure to avoid exciton quenching was made up of a double emitting layer of mCBP:5CzCN (20 nm: 5 wt%)/mCBP:$Ir(dbi)_3$ (20 nm: 5 wt%). Hole only device structure was ITO (50 nm)/HATCN (10 nm)/BPBPA or TAPC (80 nm)/HATCN (10 nm)/Al (200 nm) and electron only device structure was ITO (50 nm)/Ca (10 nm)/TPBI or BmPyPb (80 nm)/Ca (10 nm)/Al (200 nm). In order to investigate the effect of HTL/EML interface on EML, hole only devices were ITO/HATCN (10 nm)/HTMs (BPBPA or TAPC) (30 nm)/mCBP: Ir (dbi)3 (20 nm: 50%)/BPBPA:HATCN(10 nm:30%)/Al (200 nm). In order to investigate the effect of EML/ETL interface on EML, electron only devices were ITO/Ca (5 nm)/TPBI (10 nm)/mCBP:5CzCN (20 nm:50%)/ETMs (TPBI or BmPyPb) (25 nm)/Ca (5 nm)/Al (200 nm). Since $Ir(dbi)_3$ and 5CzCN are strong carrier traps, the doping concentration was as high as 50% for carrier transport.

2.2. Measurements

Device evaluation method was voltage sweep measurement of current density, luminance, and electroluminescence (EL) spectrum at an interval of 0.5 V. Keithley 2400 electrical source unit and CS 2000 (Minolta Co.) optical measurement unit were used for the EL performance test. The photoluminescence (PL) spectra of single carrier devices were measured using the ultraviolet (UV) lamp (365 nm, 1.4 mW/cm^2) and CS 2000 (Minolta Co.) spectroradiometer. Lifetime test method was constant current driving of the phosphorescent OLEDs at an initial luminance of 1000 cd/m^2.

3. Results and discussion

BPBPA and TAPC were chosen as HTMs to study the degradation process because BPBPA is a relatively stable HTM and TAPC is an unstable HTM in terms of device lifetime. In the case of ETMs, TPBI and BmPyPb were selected as TPBI is a relatively robust ETM and BmPyPb is a poor ETM in terms of device lifetime. The two HTMs and two ETMs were introduced to construct blue phosphorescent OLEDs (PHOLEDs) and TADF OLEDs to examine the origin of degradation by HTMs and ETMs.

Firstly, the stability of the HTMs and ETMs was investigated by comparing hole and electron stability of the materials, respectively. HTM stability was analyzed by driving hole only devices of HTMs at a constant current density of 10 mA/cm^2 (Fig. 1(a)). Monitoring of the driving voltage according to operation time of the hole only devices stated that BPBPA is much more stable than TAPC from the large

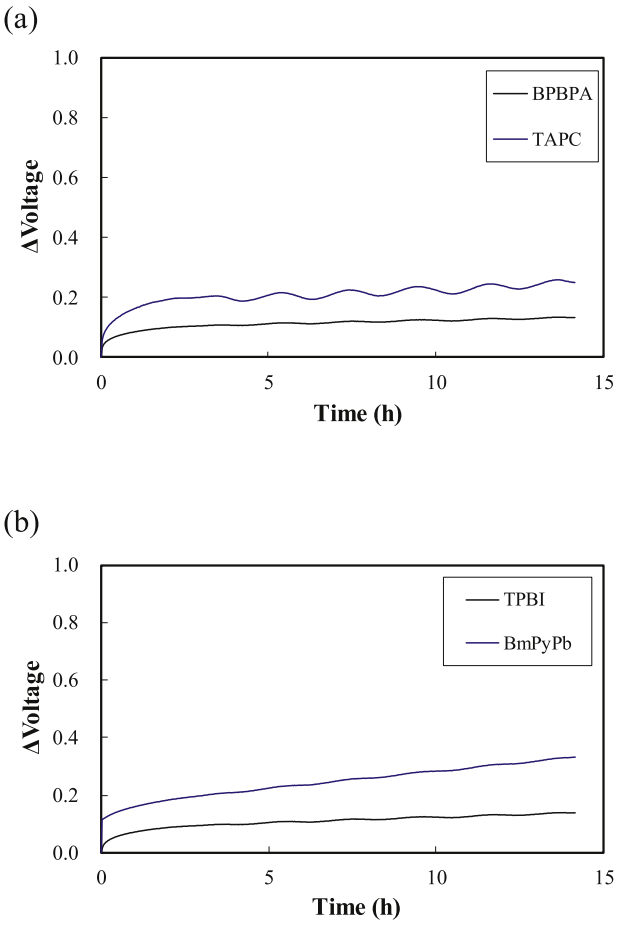

Fig. 1. Single carrier stability results of hole only devices of BPBPA and TAPC (a) and electron only devices of TPBI and BmPyPb.

voltage change of TAPC according to aging time because the voltage change is induced by material degradation. Analogously, stability test data of ETMs in Fig. 1(b) show that TPBI is better than BmPyPb because the voltage rise during driving of TPBI electron only devices is much smaller than that of BmPyPb electron only devices. From the single carrier stability test data, it can be clearly seen that BPBPA is more robust than TAPC to the hole stress, while TPBI is more stable than BmPyPb to the electorn stress.

Based on the single carrier stability data of HTMs and ETMs, the lifetime of blue PHOLEDs and TADF OLEDs was investigated according to the HTMs and ETMs of the devices which are paired in four different combinations. The emitting layer of the PHOLEDs was hole trapping type mCBP:$Ir(dbi)_3$ and that of the TADF OLEDs was electron trapping type mCBP:5CzCN [19]. The device structure of the PHOLEDs and TADF OLEDs is schematized in Fig. 2 along with energy levels and chemical structures of the materials. Lifetime testing results of the PHOLEDs and TADF OLEDs are summarized in Figs. 3 and 4. Luminance changes of the devices at a constant current driving mode are presented. The lifetime of the PHOLEDs was sensitive to the HTMs and the blue PHOLEDs with BPBPA showed much longer lifetime than those with TAPC. Whereas, the ETMs had little effect on the lifetime of the devices although TPBI was more stable than BmPyPb in the electron only device stress test. The effect of the HTMs and ETMs on the lifetime of the TADF OLEDs was quite different from that of the PHOLEDs. The lifetime of the TADF OLEDs was dominated by the ETMs and was not influenced by the HTMs. Relatively long lifetime was obtained when