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Development of highly stable organic electroluminescent devices with a doped co-host emitter system ☆

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Abstract

Efficient red organic light-emitting devices based on the fluorescent dye "4-(dicyanomethylene)-2-*t*-*butyl*-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) doped in co-host emitter (CHE) systems of rubrene/*tris*(8-hydroxyquinolinato)aluminum (Alq_3) [60/40] and of 9,10-*di*(2-naphthyl)anthracene (ADN)/Alq_3 [60/40] which achieved a luminance efficiency of 4.2–5.5 cd/A at 20 mA/cm^2 with Commission Internationale d'Eclairage coordinates of $[0.64, 0.35]$–$[0.62, 0.37]$. At high rubrene or ADN concentration (>60%), this DCJTB doped CHE system has the advantage of alleviating the current-induced fluorescence quenching problem often encountered in red organic electroluminescence (EL) devices and greatly improves the EL efficiency over a wide range of drive current conditions.

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Keywords: Organic electroluminescence; OLED; Doped co-host emitter; Red dopant; Fluorescent; Bipolar; Efficient; Stable

1. Introduction

One of the key enablers in the development of organic light-emitting device (OLED) technology can be attributed to the discovery of the guest-host doped emitter system [1]. This is because a single host material with optimized transport and luminescent properties may be used together with a variety of highly fluorescent dopants leading to electroluminescence (EL) of desirable hues with high efficiencies and enhanced operational stability [2]. This doping principle has recently been successfully extended to the exploitation of highly phosphorescent materials leading to nearly 100% internal EL efficiency [3]. But, for the fluorescent red dopant – 4-(dicyanomethylene)-2-*t*-*butyl*-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, known as DCJTB [4] used in many of today's OLED displays on the market, this simple doping scheme in host *tris*(8-hydroxyquinolinato)aluminum (Alq_3) has proven to be inadequate to meet simultaneously all of the requirements of color, efficiency and stability of the red emitter for full color OLED applications. Despite of the fact that DCJTB is an excellent red fluorescent dye with solution photoluminescence $\lambda_{max} \sim 630$ nm and a quantum efficiency $\eta > 90\%$, the optimally doped EL in Alq_3 produces an orange emission that is often contaminated by the residual green emission from the host Alq_3. Although the color saturation of DCJTB can be improved by high level of doping, its luminance efficiency can be greatly compromised due to the onset of concentration quenching. As a result, red color approaching Commission Internationale d'Eclairage (CIE) coordinates ($x = 0.65$, $y = 0.35$) can only be obtained at dopant concentration of higher than 4–5% when the luminance has dropped well below its peak. By dispersing 5% of rubrene as a red *emitting assist dopant* with 2% DCJTB in Alq_3, Hamada and coworkers at Sanyo [5] were able to achieve a luminance

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efficiency of 2.1 cd/A with $\mathrm{CIE}_{x,y} = [0.64, 0.35]$. Subsequently, the Sanyo/Kodak team discovered [6] that by adding 6% of N,N'-*bis*(1-naphthyl)-N,N'-diphenyl-1,1′-biphenyl-4,4′ diamine (NPB) as hole-trapping dopant to the above emitting system, its efficiency could be further improved to 2.8 cd/A at 20 mA/cm^2 and a red chromaticity coordinate of $\mathrm{CIE}_{x,y} = [0.65, 0.34]$ was also obtained. The encapsulated device structure disclosed in that report showed a remarkable projected operational half-life of 8000 h with a starting luminance of 550 cd/m^2.

Instead of adding *assist dopants* in the emitter, we have undertaken a different approach to address the doped red-emitter issue by studying the effect of changing the nature of host system on the EL efficiency, color and stability of DCJTB doped devices. We define our system as doped *co-hosted emitter* (CHE) that is composed of doping one single dopant (such as DCJTB) in *two* host emitters in which one is capable of bipolar carriers transport and both of them should be emissive and be able to resist concentration quenching and sensitize the dopant (DCJTB) efficiently. We will show that by adjusting the ratio of these two host emitters, the EL efficiency, color as well as stability can be dramatically improved. Moreover, by using this CHE system nearly all of the problematical issues that have been plaguing the DCJTB/$\mathrm{Alq_3}$ doped red emitter, such as the current-induced fluorescence quenching, device longetivity and color shift as well as the low luminance efficiency and color saturation can also be resolved. We will track and describe herewith the development of DCJTB doped CHEs and compare the EL performance of co-host systems of rubrene/$\mathrm{Alq_3}$ and 9,10-*di*(2-naphthyl)anthracene (ADN)/$\mathrm{Alq_3}$.

2. Experimental

The CHE consists of a mixture of either rubrene/$\mathrm{Alq_3}$ or ADN/$\mathrm{Alq_3}$ doped with 2% DCJTB. The CF_x, NPB, and $\mathrm{Alq_3}$ were used as the hole injection material [7], hole transport, and electron transport material, respectively, to form OLEDs of the following optimized device architecture as shown in Fig. 1: [indium-tin-oxide (ITO) anode (200 nm)/CF_x (5 nm)/NPB (120 nm)/CHE (30 nm)/$\mathrm{Alq_3}$ (50 nm)/LiF (1 nm)-Al (200 nm) cathode]. Prior to organic deposition, the ITO coated glass plate was thoroughly cleaned by scrubbing, sonication, vapor degreasing, and oxygen plasma treatment. Devices were fabricated under the vacuum of about 10^{-6} Torr in a thin-film evaporation coater following a published protocol [8]. All devices were hermetically sealed prior to testing. The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 0.09 cm^2. The current–voltage–luminance characteristics of the devices were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled programmable DC source. The lifetime measurements were performed in a glove box at a constant current density of 20 mA/cm^2.

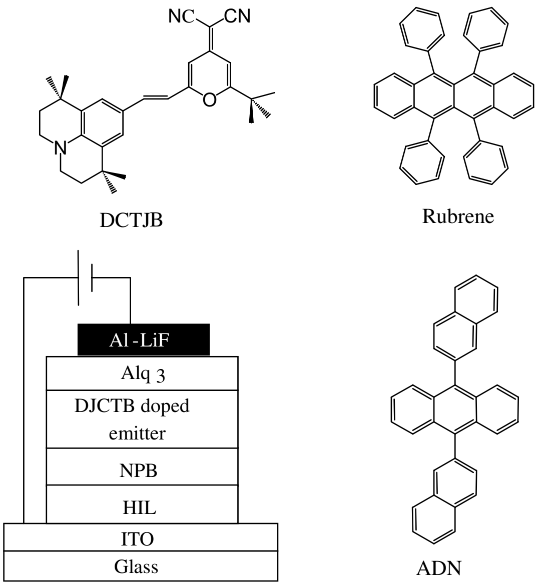

Fig. 1. Structure of doped device and dopant and co-host emitter materials.

3. Result and discussion

DCJTB doped rubrene/$\mathrm{Alq_3}$ of 60/40 co-host emitter (CHE) system was first disclosed at IDW'02 in which an EL efficiency of 4.4 cd/A and 2 lm/W at 20 mA/cm^2 and 6.8 V with a red $\mathrm{CIE}_{x,y}$ coordinate of [0.65, 0.35] was achieved at 2% doping [9]. We proposed also in the rubrene/$\mathrm{Alq_3}$ co-host system, the bipolar rubrene at >60% concentration acts as major charge carriers which can remove excess holes that are produced at high current density and thus reduces the propensity for the formation of $[\mathrm{Alq_3}]^{+\cdot}$ which is a well-known quenching species that can also lead to device instability [10]. The red emission of DCJTB can result either from Förster energy transfer from rubrene or by direct charge trapping at the dopant site. Since the bandgap energy of rubrene ($E_\mathrm{g} \sim 2.2$ eV) lies in-between those of $\mathrm{Alq_3}$ (2.8 eV) and DCJTB (2.1 eV), it is not clear as to whether a cascade energy transfer scheme is a necessary condition for the co-host system to operate in the DCJTB doped emitter.

To remove doubts that rubrene could serve as the medium for cascade energy transfer from $\mathrm{Alq_3}$-rubrene-DCJTB, we broadened the material selection to include the wide bandgap, bipolar blue host material, ADN [11] and demonstrated recently in SID'03 that ADN can be used just effectively as the major host component in combination with $\mathrm{Alq_3}$ in DCJTB-doped CHE emitter [12]. Fig. 2 compares the luminance yield (cd/A) and drive voltage vs. rubrene and ADN concentration (in