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

Tswen-Hsin Liu [a], Chung-Yeh Iou [b], Chin H. Chen [b,*]

[a] Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, 30050, Taiwan, ROC
[b] Microelectronics and Information Systems Research Center, Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan, ROC

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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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

efficiency of 2.1 cd/A with $CIE_{x,y}$ = [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/cm² and a red chromaticity coordinate of $CIE_{x,y}$ = [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/m².

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/Alq₃ 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/Alq₃ and 9,10-*di*(2-naphthyl)anthracene (ADN)/Alq₃.

2. Experimental

The CHE consists of a mixture of either rubrene/Alq₃ or ADN/Alq₃ doped with 2% DCJTB. The CF_x, NPB, and Alq₃ 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)/Alq₃ (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 cm². 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
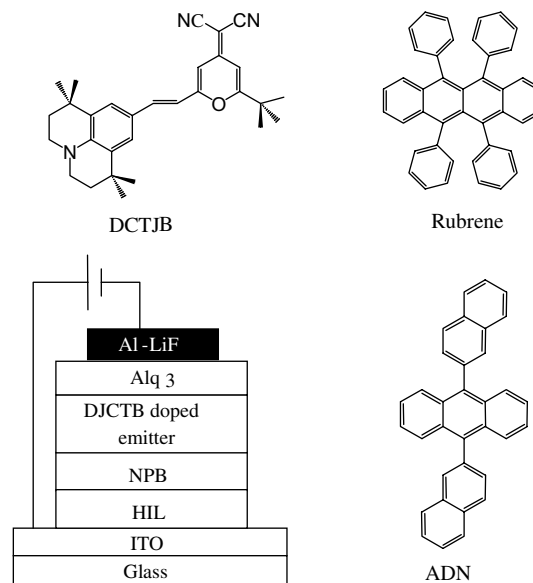

Fig. 1. Structure of doped device and dopant and co-host emitter materials.

source. The lifetime measurements were performed in a glove box at a constant current density of 20 mA/cm².

3. Result and discussion

DCJTB doped rubrene/Alq₃ 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/cm² and 6.8 V with a red $CIE_{x,y}$ coordinate of [0.65, 0.35] was achieved at 2% doping [9]. We proposed also in the rubrene/Alq₃ 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 $[Alq_3]^{+\cdot}$ 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 ($E_g \sim 2.2$ eV) lies in-between those of Alq₃ (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 Alq₃-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 Alq₃ in DCJTB-doped CHE emitter [12]. Fig. 2 compares the luminance yield (cd/A) and drive voltage vs. rubrene and ADN concentration (in
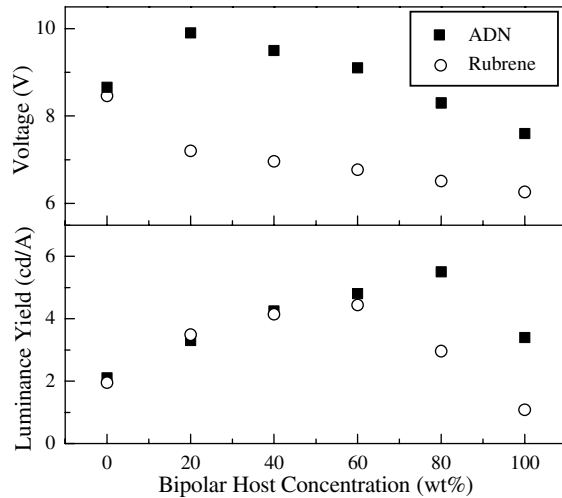
Fig. 2. Efficiency and drive voltage dependency on ADN (■) and rubrene (○) concentration in Alq₃ of 2% DCJTB doped CHE devices.

Fig. 3. Efficiency of 2% DCJTB doped CHE devices vs. drive current density where (■) is ADN/Alq$_3$ = 60/40; (○) is rubrene/Alq$_3$ = 60/40; (△) is single host of Alq$_3$ (Inset: EL spectra of ADN/Alq$_3$ (60/40) CHE devices in various drive current conditions.).

wt%) of a series of 2% doped DCJTB devices. In both cases, we find that the device drive voltage decreases steadily with respect to increasing rubrene or ADN concentration while the luminance efficiency tops out at ∼60% for rubrene and ∼80% for ADN, respectively. The decrease in drive voltage of both devices with increasing rubrene or ADN concentration in the co-host mixture is apparently due to the enhanced bipolar transport nature of rubrene or ADN. The slightly higher voltage observed in doped ADN/Alq₃ co-host emitters could be attributed to the higher LUMO level of ADN (−2.6 eV) as compared to that of rubrene (−3.2 eV) and the high luminance efficiency of ADN/Alq₃ CHE is believed to arise from the wider bandgap energy of ADN. Detailed EL performance data of representative devices are listed in Table 1. The best EL performance of these 2% DCJTB doped ADN/Alq₃ co-host emitters is found in co-host ratio of 60/40 which achieved a luminance efficiency of 4.8 cd/A and a power efficiency of 1.66 lm/W with a color coordinate of CIE$_{x,y}$ = [0.64, 0.36] driven at a dc current density of 20 mA/cm² and 9.1 V. This efficiency is believed to be one of the best ever reported for an electrofluorescent red OLED emitter. We noted also that, although device with 80% ADN has the
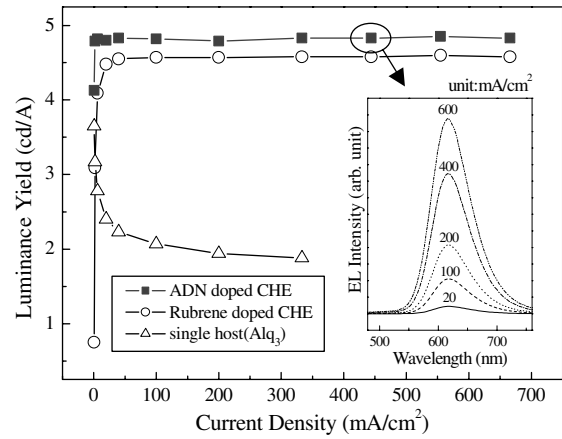
highest luminance efficiency of 5.5 cd/A, the red color saturation is compromised due to the solvent-induced polarization effect[13] which causes the EL emission of DCJTB to shift to orange at CIE$_{x,y}$ = [0.62, 0.37].

Fig. 3 shows the plot of luminance efficiency vs. drive current density for two representative 2% doped DCJTB CHE devices of rubrene/Alq₃ and ADN/Alq₃ with co-host ratio of 60/40 as indicated in Table 1. It appears from the profile that only at co-host mixtures of ADN/Alq₃ and rubrene/Alq₃ ratio reach 60/40, can the cd/A response be obtained independent of drive current density. From the inset, it is also shown that the EL spectra of 2% DCJTB doped ADN/Alq₃ (60/40) CHE will not be effected by the driving current condition. This means that the usual quenching phenomenon of DCJTB doped Alq₃ device at high drive current density is effectively suppressed by the presence of large proportion of the bipolar transport rubrene or ADN in the CHE system. It also suggests that the presence of large amount of rubrene or ADN in DCJTB doped device can also remove the excess hole that is produced at high current density and thus reduces the propensity for the formation of [DCJTB]⁺· which has been identified as a potential quenching species that can also lead to device instability [14].

Table 1
EL performance of 2% DCJTB doped CHE system

Device	CHE Composition	Voltage (V)	CIE		LumYield (cd/A)	Efficiency (lm/W)
			X	Y		
A	Rub:Alq$_3$ = 80:20	6.5	0.63	0.37	3.0	1.5
B	Rub:Alq$_3$ = 60:40	6.8	0.65	0.35	4.4	2.1
C	Rub:Alq$_3$ = 20:80	7.2	0.66	0.34	3.5	1.5
D	ADN:Alq$_3$ = 80:20	8.3	0.62	0.37	5.5	2.1
E	ADN:Alq$_3$ = 60:40	9.1	0.64	0.36	4.8	1.7
F	ADN:Alq$_3$ = 20:80	9.9	0.65	0.35	3.3	1.1
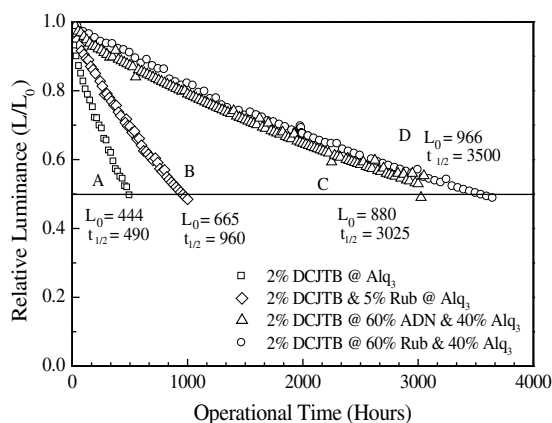
Fig. 4. Operational stability of 2% DCJTB doped CHE devices at 20 mA/cm^2. A ($\square$) = Alq$_3$ single host; B ($\diamond$) = dual dopant of 5% rubrene in Alq$_3$; C ($\triangle$) = ADN/Alq$_3$ (60/40) CHE; D ($\bigcirc$) = rubrene/Alq$_3$ (60/40) CHE.

Since the CHE system can efficiently suppress the intrinsic quenching effect of DCJTB doped OLEDs, device operational lifetime is expected to improve. Indeed, results from the device operational stability tests for 2% DCJTB doped OLEDs, driven at 20 mA/cm^2, for compositions of emission layer of **A** [Alq$_3$] = [100], **B** [rubrene:Alq$_3$] = [5:95], **C** [ADN:Alq$_3$] = [60:40] and **D** [rubrene:Alq$_3$] = [60:40], are shown in Fig. 4. Their initial luminances (L_0) for each emitter system of **A**, **B**, **C** and **D** are 444, 665, 880, and 966 cd/m^2, respectively. Assuming the scalable Coulombic degradation law would hold [8], the half-life ($t_{1/2}$) of 2% DCJTB doped co-host emitter is projected to be 33,810 h for rubrene/Alq$_3$ [60:40] and 26,620 h for ADN:Alq$_3$ [60:40] upon driving at initial luminance L_0 of 100 cd/m^2.

4. Conclusion

We have developed what appears to be one of the most efficient and stable red devices ever reported for the fluorescent DCJTB doped emitter at 4.8 cd/A driven at 20 mA/cm^2 and 9.1 V with a CIE$_{x,y}$ red color coordinate of [0.64, 0.36] and a projected operational $t_{1/2}$ life time of ~30,000 h with normalized initial L_0 of 100 cd/m^2. By doping DCJTB into the novel co-hosted matrix emitting system of ADN/Alq$_3$ as well as rubrene/Alq$_3$ at a ratio of 60/40, we have also successfully eliminated the problem of luminescence quenching at high drive voltage and achieved a "flat" cd/A vs. J response that is highly desirable for passive as well as active matrix full color OLED flat panel display applications.

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