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Improved performances of red organic light-emitting devices by co-doping a rubrene derivative and DCJTB into tris-(8-hydroxyquinoline) aluminum host

Tianle Li [a,b], Wenlian Li [b,*], Xiao Li [b], Bei Chu [b,*], Zisheng Su [b], Liangliang Han [b], Yiren Chen [b], Zhizhi Hu [c], Zhiqiang Zhang [c]

[a] Physics Department, School of Science, Maoming University, Maoming 525000, People's Republic of China
[b] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China
[c] Optic Photo-Electronic Materials and Research Development Center, Liaoning University of Science and Technology, Anshan 114044, People's Republic of China

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ABSTRACT

Performances of red organic light-emitting device were improved by co-doping 2-formyl-5,6,11,12-tetraphenylnaphthacene (2FRb) and 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetra-methyljulolidyl-9-enyl)-4H-pyran (DCJTB) in tris-(8-hydroxyquinoline) aluminum (Alq_3) host as the emitting layer. The device with 1 wt% DCJTB and 2.4 w% 2FRb in Alq_3 host gave a saturated red emission with CIE chromaticity coordinates of (0.65, 0.35) and a maximum current efficiency as high as 6.45 cd/A, which are 2 and 2.4 fold larger than that of the device with 1 wt% DCJTB (3.28 cd/A) in Alq_3 host and the device with 2.4 wt% 2FRb (2.72 cd/A) in Alq_3 host at the current density of 20 mA/cm^2, respectively. The improvement could be attributed to the effective utilization of host energy by both energy transfer and trapping in the electroluminescence process and the depression of concentration quenching between the dopants molecules.

1. Introduction

Organic light-emitting devices (OLEDs) have attracted more and more attentions for their potential applications in flat panel displays and solid state lighting [1–3]. In such applications, red emission having high luminance and saturated color is required. Red OLEDs are often fabricated by doping a red dye into a host material, the emission obtained in such doping systems, however, was generally not the pure red but the orange due to the partial excitation of the host and the poor energy transfer from the host to the guest [4]. Recently, red OLEDs were fabricated by doping two guest dyes in one host as the emitting layer to improve the color purity and the device efficiency [4,5]. Hamada et al. [4] co-doped rubrene and [2-methyl-6-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene] propanedinitrile (DCM2) into tris-(8-hydroxyquinoline) aluminum (Alq_3) host, in which rubrene was used as the assistant dopant to assist the energy transfer from Alq_3 to DCM2 to improve the color purity of red emission. D'Andrade et al. [5] reported that *fac* tris(2-phenylpyridine) iridium [Ir(*ppy*)$_3$] was used as a sensitizer to assist the energy transfer from the 4,4′-*N*,*N*′-dicarbazole-biphenyl host to DCM2. Compared with assistant dopant or sensitizer to aid the energy from the host to the dopant, introduction of two dopants with different electroluminescence (EL) mechanisms in one host as the emitting layer is also a feasible method to take full use of host energy and further to improve the performances of the device.

In this paper, we fabricated highly efficient red OLED with saturated red emission by doping two red-emitting dopants, 2-formyl-5,6,11,12-tetraphenylnaph-thacene (2FRb) and DCJTB, into Alq_3 host, in which 2FRb is a bipolar rubrene derivative inherited some good properties from rubrene, especially trapping in EL process. The emission of this co-doped device was from 2FRb and DCJTB dye simultaneously rather than one species. A maximum current efficiency of 6.45 cd/A and saturated red emission with CIE coordinates of ($x=0.65$, $y=0.35$) in 1 wt% DCJTB and 2.4 wt% 2FRb co-doped device were attained.

2. Experimental

Fig. 1 shows the chemical structures of DCJTB and 2FRb and the schematic energy level diagram corresponding to the device structure. 2FRb was synthesized and purified in our lab and other chemicals were commercially purchased without further purification. All materials were thermally deposited in succession without breaking vacuum ($\sim 3\times10^{-4}$ Pa) onto a pre-cleaned indium tin oxide (ITO)-coated glass substrate with sheet resistance of 20 Ω/sq. The substrates were routinely cleaned by

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* Corresponding authors. Tel./Fax: +86 431 6176345.
E-mail addresses: wllioel@yahoo.com.cn (W. Li), beichubox@hotmail.com (B. Chu).

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ultrasonic solvent bath and then exposed to an UV–ozone ambient prior to loading into a vacuum chamber. Thermal deposition rates of organic materials, LiF, and Al were ~1, ~1, and 10 Å/s, respectively. Absorption spectra of 2FRb and DCJTB in $CHCl_3$ solutions and photoluminance (PL) spectra of neat Alq_3 solid film and electroluminescent (EL) spectra with CIE coordinates were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The data of luminance–current–voltage (*L*–*I*–*V*) were measured with a 3645 dc power supply combined with a 1980 A spot photometer. All measurements were performed in air without encapsulation. The emitting area was 2×2 mm^2. The device structure is ITO/2-TNATA (10 nm)/NPB (40 nm)/Alq_3: *x* wt% DCJTB: *y* wt% 2FRb (30 nm)/ BCP (10 nm)/Alq_3(40 nm)/ LiF (0.5 nm) /Al (200 nm). Here, 2-TNATA, NPB and BCP denote 4,4′,4″-tris(*N*-(2-naphthyl)-*N*-phenyl-amino)triphenylamine, 4, 4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl and 2,9-dimethyl-4,7-diphenyl-phenanthroline, respectively. 2-TNATA and NPB serve as hole injecting and transporting layers, BCP acts as hole and exciton blocker, LiF and adjacent Alq_3 are electron injection and transporter, here *x* and *y* is abbreviated as [*x*, *y*] for fabricated device structure, $x=0.0$, 1.0, 2.0, 3.0, 3.4, 4 for the concentration of DCJTB and $y=$ 0.0, 0.8, 1.6, 2.4, 3.2, 3.4 for the concentration of 2FRb, respectively. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of 2FRb were determined with a cyclic voltammeter and calculated with the absorption spectra and LUMO and HOMO levels of other materials are cited from Refs. [3,4,6], respectively.

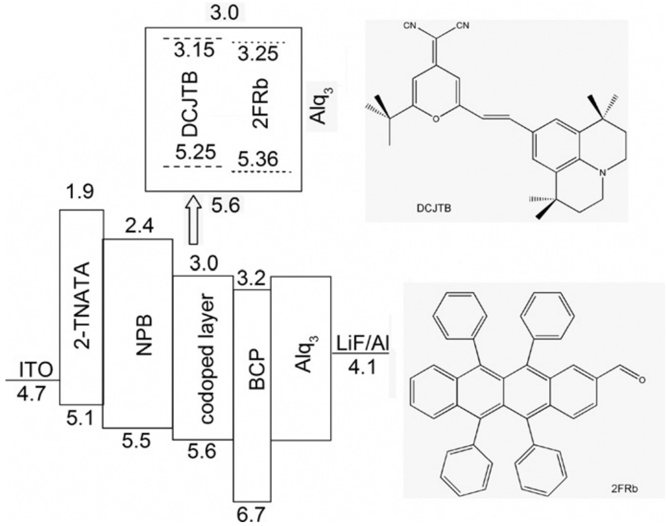

Fig. 1. Chemical structures of DCJTB and 2FRb as well as the schematic energy level diagram corresponding to the device structure.

3. Results and discussions

The EL performances and the evolution of the CIE coordinates with voltages are summarized in Table 1 and Fig. 2 plots the current efficiency–current density characteristics of single-doped [1.0, 0.0], [0.0, 2.4] devices and co-doped [1.0, 2.4] devices. We can find that at a current density of 20 mA/cm^2, co-doped [1.0, 2.4] device gave a maximum efficiency of 6.46 cd/A, which is almost two times higher than that of single-doped [1.0, 0.0] (DCJTB, 3.28 cd/A) or [0.0, 2.4] (2FRb, 2.72 cd/A) devices. The current efficiencies of the co-doped device maintained at 2.89 at 100 mA/cm^2 and 2.70 cd/A at 200 mA/cm^2, which are still 50% and 58% higher than that of the [1.0, 0.0] and [0.0, 2.4] devices, respectively. Also, compare EL intensities of device [3.4, 0.0] and device [1.0, 0.0] or device [0.0, 2.4] and device [0.0, 3.4] from Table 1, we can find that highly doped device shows lower luminance due to the concentration quenching. However, the efficiency of the optimal co-doped [1.0, 2.4] device (total concentration of 3.4 %) is 2.4 and 2.7 times more than that of device [3.4, 0.0] and device [0.0, 3.4], respectively. This finding indicates that the concentration quenching in the optimal devices was successfully suppressed. It also proves that there should be two different mechanisms in the EL process, trapping and energy transfer mechanisms, which lead to the high efficiency from the co-doped device.

Fig. 3 (a) shows the EL spectra of red emissive OLEDs vary with doping ratio and Fig. 3 (b) shows the EL spectra of device [1, 2.4] vary with voltage. From Fig. 3 (a), we can observe that there are two emission peaks at 612 and 617 nm originated from respective single-doped DCJTB and 2FRb devices, we also find there is a slight emission peaking around 530 nm in device [1.0, 0.0], which should be attributed to the emission of the Alq_3 host, indicating that the host energy was not fully utilized. When the doping concentration of DCJTB increased while that of 2FRb was fixed at optimized 2.4%, the emission from two dopants rises and that from host gradually disappears, the emission peak red shifted from 617 to 628 nm, which is determined by the doping level of DCJTB. However, the color of the co-doped device [1.0, 2.4] shows

Table 1
EL performances of the devices.

DCJTB (%)	2FRb (%)	λ_{max}[a] (nm)	η_c[b] (cd/A)	Luminance (cd/m^2)	CIE coordinates (*x*, *y*) at varying voltage		
					6 V	12 V	18 V
0	2.4	617	2.72	4950	(0.61, 0.38)	(0.60, 0.39)	(0.59, 0.40)
0	3.4	622	2.42	3100	(0.64, 0.35)	(0.64, 0.35)	(0.63, 0.36)
1	0	612	3.28	10,800	(0.62, 0.37)	(0.60, 0.39)	(0.59, 0.40)
3.4	0	624	2.47	3698	(0.65, 0.35)	(0.64, 0.35)	(0.62, 0.37)
1	2.4	617	6.45	5777	(0.65, 0.35)	(0.63, 0.37)	(0.61, 0.39)
2	2.4	619	5.10	3319	(0.63, 0.37)	(0.64, 0.36)	(0.62, 0.38)
3	2.4	626	2.97	2550	(0.66, 0.34)	(0.65, 0.35)	(0.62, 0.38)
4	2.4	628	2.08	1340	(0.66, 0.34)	(0.65, 0.35)	(0.65, 0.35)
1	0.8	612	5.18	3320	(0.64, 0.36)	(0.62, 0.38)	(0.61, 0.39)
1	1.6	615	5.40	3600	(0.64, 0.36)	(0.62, 0.38)	(0.58, 0.41)
1	2.4	617	6.45	5777	(0.65, 0.35)	(0.63, 0.37)	(0.61, 0.39)
1	3.2	624	4.40	2778	(0.66, 0.34)	(0.64, 0.36)	(0.63, 0.37)

[a] λ_{max}: Peak emission wavelength.
[b] η_c: the current efficiency.

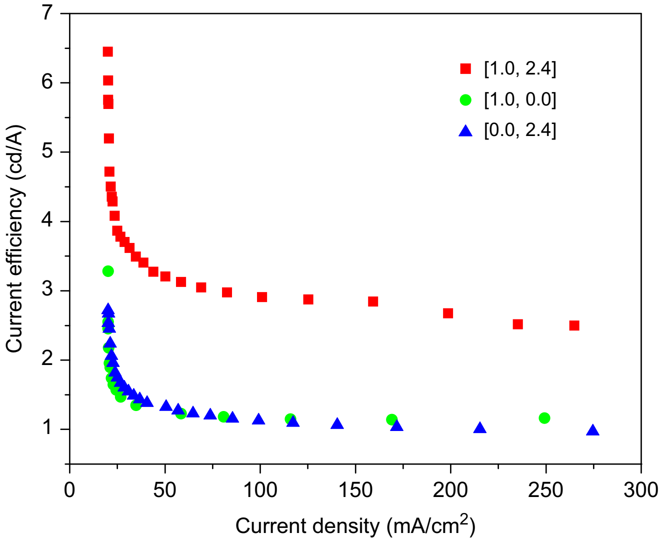

Fig. 2. Current efficiency–current density characteristics of device [1.0, 2.4], device [1.0, 0.0] and device [0.0, 2.4].

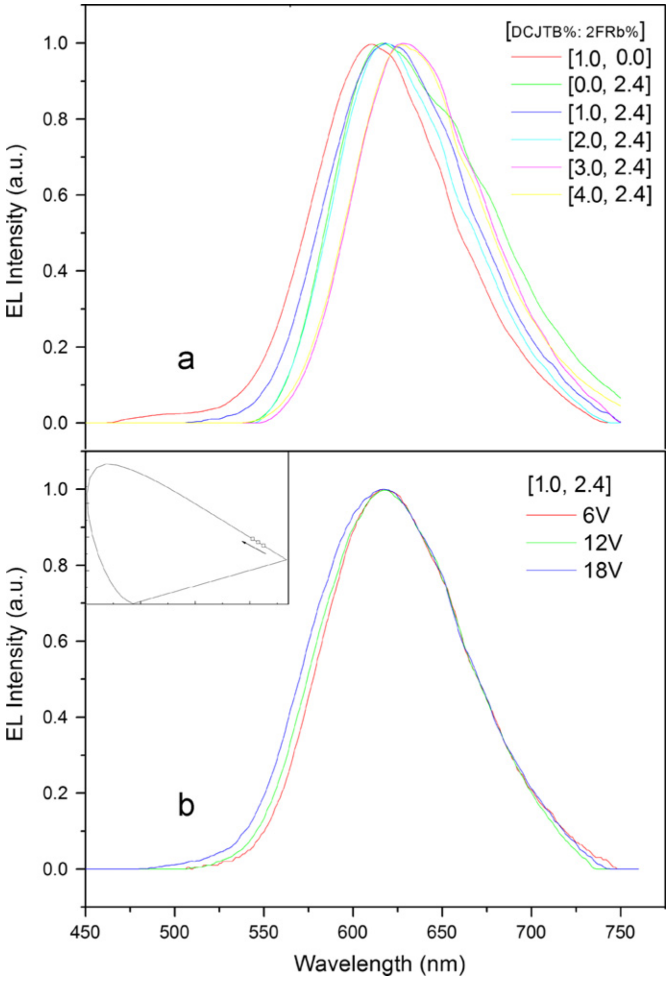

Fig. 3. EL spectra of red OLEDs vary with doping ratio (a) and the EL spectra of [1, 2.4] devices vary with voltage (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

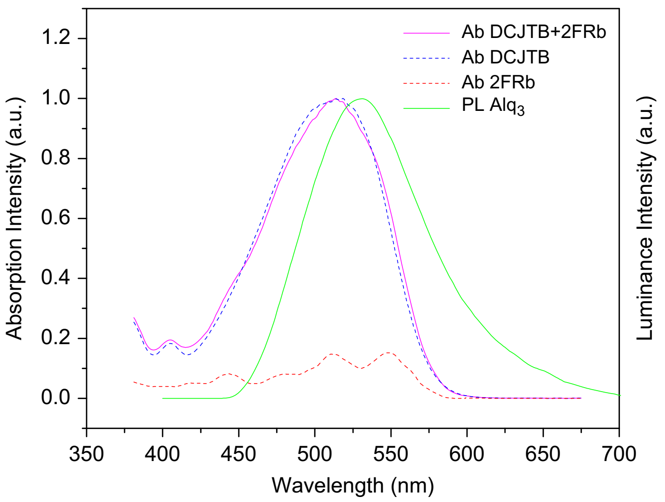

Fig. 4. The absorption (Ab) spectra of DCJTB, 2FRb and their 1:1 mix in CHCl$_3$ solutions and PL spectrum of neat Alq$_3$ film.

better stability compared with device [1.0, 0.0] and device [0.0, 2.4]. From Fig. 3(b), the emission spectra peak at 617 nm and there is a slight blue-shift with the increase of voltage, made the CIE coordinates move from (0.65, 0.35) to (0.61, 0.39) indicated in the inset of Fig. 3(b), might be caused by the exciton de-trapping [6] on 2FRb molecule at higher voltage.

To further explore the EL mechanism of the DCJTB and 2FRb in Alq$_3$ host, we investigated the absorption spectra of DCJTB, 2FRb and their 1:1 mixture in CHCl$_3$ solutions and the PL spectrum of Alq$_3$ film with excitation of 365 nm light, as shown in Fig. 4. It can be seen that the absorption of the mixture in solution originates apparently from a simple addition of the two respective absorptions of DCJTB and 2FRb but it almost the same with that of DCJTB due to weak absorption band around 530 nm of 2FRb, indicating Förster energy transfer from Alq$_3$ to DCJTB should be the main EL mechanism due to a large spectral overlap between absorption spectrum of DCJTB and PL spectrum of Alq$_3$.

In 2FRb only doped device, the HOMO and LUMO levels of 2FRb within that of the host (see Fig. 1) and the emission peak does not shift with voltage indicating the charge trapping is the main EL mechanism [7]. In DCJTB only doped device, the polarization-induced spectral shifts [8] made the EL color shift from orange to red with the increase of DCJTB concentration, when 2FRb was added into the system, it might do not only intermediate the energy transfer from Alq$_3$ to DCJTB [4], but charge directly traps on 2FRb molecules then emits. The emissions of 2FRb contributed to the EL of co-doped device. The slight difference of excitation energy band gap between DCJTB (2.10 eV) and 2FRb (2.11 eV) made the energy transfer from 2FRb to DCJTB be reversible and the competition process of energy transfer from the host to 2FRb or DCJTB, the host energy be utilized more adequately [9]. On the other hand, charge trapping is a faster process than that of Förster energy transfer [10], which might weaken the interaction between the excitons of DCJTB and 2FRb molecules, so that aggregation effect leading to concentration quenching might be avoided so that the EL properties of the device [1.0, 2.4] was obviously improved.

4. Summary

In summary, co-doped devices incorporating two red emitting dyes, 2FRb and DCJTB, into Alq$_3$ host were fabricated and the color purity and the efficiency of the red OLED were improved. The doping of two dyes with different EL mechanisms in one host is to fully utilize the energy of the host, quench the emission from host further to avoid the notorious of color and also to improve the EL efficiency simultaneously. As a result, a maximum current efficiency of

6.45 cd/A and a saturated red emission with color CIE coordinates of ($x=0.65$, $y=0.35$) of 1 wt% DCJTB and 2.4 wt% 2FRb co-doped device were attained. So the co-doping technique provides an effective way to overcome the concentration quenching and hence to improve the EL efficiency and color purity.

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