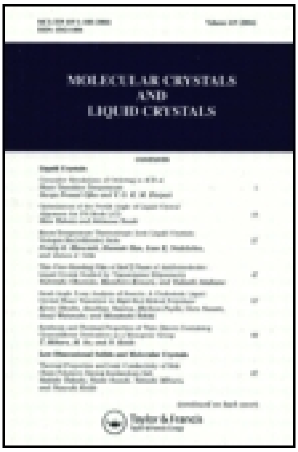

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Red Fluorescent 4-(Dicyanomethylene)-2- (1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1,2,2,7,7-hexamethyljulolidyl-9-enyl)-4H-pyran (DCHMJPB) for Organic Light-Emitting Diodes (OLEDs)

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Red Fluorescent 4-(Dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1,2,2,7,7-hexamethyljulolidyl-9-enyl)-4H-pyran (DCHMJPB) for Organic Light-Emitting Diodes (OLEDs)

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An efficient red fluorescent compound, 4-(Dicyanomethylene)-2-(1-pentylbicyclo-[2,2,2]oct-4-yl)-6-(1,1,2,2,7,7-hexamethyljulolidyl-9-enyl)-4H-pyran (DCHMJPB) containing two additional methyl groups on julolidine moiety and 1-pentylbicyclo-[2,2,2]octyl group on pyran moiety, was synthesized and characterized. In this red emitter, the bulky groups such as two additional methyl groups and 1-pentylbicyclo-[2,2,2]octyl group were introduced to increase the steric hindrance between the red emitters and prevent concentration quenching. In particular, in an efficient red device containing emitter DCHMJPB as a dopant, a luminous and power efficiency of 3.76 cd/A and 1.97 lm/W was achieved, respectively, at 20 mA/cm^2 with the CIE coordinates of ($x = 0.56$, $y = 0.42$) at 7.0V.

Keywords Red Fluorescence; OLED; Julolidine Derivative; DCJTB Derivative

1. Introduction

Among three primary color-emitting materials for full color organic light-emitting diodes, red fluorescent emitting materials are far from ideal in terms of efficiency and color purity [1–3]. The lack of high-performance red-light-emitting materials results from extensively π-conjugated structures, which leads to a high tendency of aggregation so-called concentration quenching [4]. Although a variety of red fluorescent materials have been widely studied for overcome this problem, most fluorescent red emitters are electron donor-π bridge-electron acceptor (D-$\pi-$A) systems including the derivatives of 4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran (DCM) [5,6]. D-π-A type materials have a remarkable advantage for the ease in fine tuning of their electroluminescent properties through the structural modifications. Thus efficient fluorescent red emitters have been developed over the past decade. Nevertheless in most DCM type emitters, concentration quenching due to excimer and exciplex formation dramatically reduces EL performance. Thus, there had been considerable efforts to developed efficient red fluorescent materials by preventing

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excimer and exciplexes formation through incorporation of sterically bulky moieties in the emitters [7].

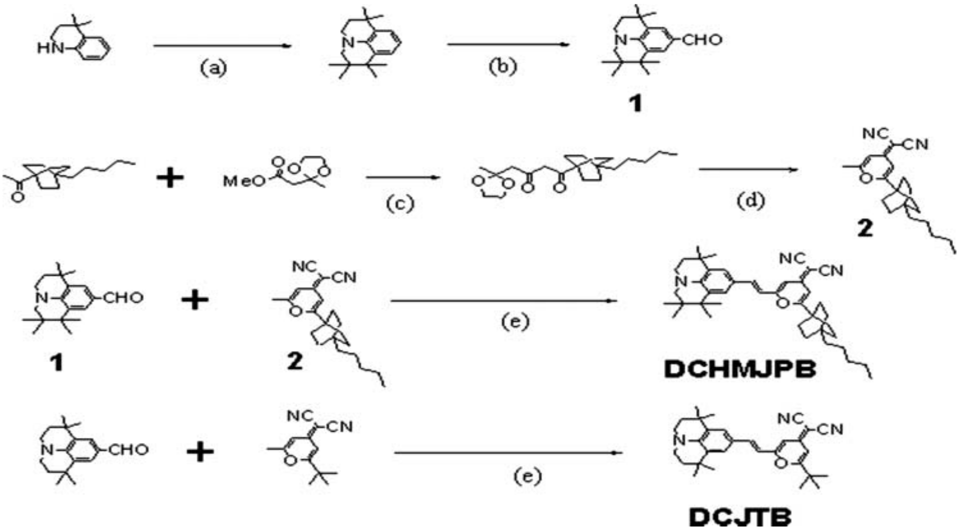
4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) represents one of the most efficient fluorescent red emitting materials for OLEDs. In DCJTB, the bulky substituent such as four methyl groups on julolidine moiety and tert-butyl group on dicyanomethylenepyran moiety of DCM backbone are incorporated to prevent concentration quenching between the emitting materials, which lead to the improved EL efficiencies of devices using them [8]. However, their EL performances still need to be improved. One possible solution to this problem is to introduce the additional bulky groups than tert-butyl and iso-propyl groups in DCJTB backbone to reduce concentration quenching and thus improve the EL efficiencies [9, 10, 11].

In this paper, we describe the synthesis and electroluminescent properties of a red fluorescent material (Dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1,2,2,7,7-hexamethyljulolidyl-9-enyl)-4H-pyran (DCHMJPB). In red emitter DCHMJPB, two additional methyl groups on julolidine moiety and 1-pentylbicyclo[2,2,2]octyl group on pyran moiety are introduced into DCJTB skeleton to increase steric hindrance between red emitters in the emitting layer of devices and thus improve the EL performances by preventing concentration quenching.

2. Experimental

2.1. Materials and Measurement

Structures and synthetic scheme of DCHMJPB and DCJTB were shown in Scheme 1. Synthesis of the red emitter DCHMJPB began with the preparation of 1,1,2,2,7,7-tetramethyljulolidine-9-carboaldehyde and 2-methyl-6-(1-pentylbicyclo[2,2,2]oct-4-yl)-4-(dicyanomethylene)-4H-pyran by following the known procedure [13]. Subsequently, Knoevenagel condensation [14] between these two intermediate in the presence of piperidine



Scheme 1. Synthesis and structures of DCHMJPB and DCJTB.

provided the red emitter DCHMJPB with the moderate yield. DCJTB was prepared by following the standard procedure [15].

The UV-Vis absorption and photoluminescence spectra of these newly designed red dopants were measured in a 10^{-5} M solution of 1,2-dichloroethane. Fluorescent quantum yields were determined in 1.2-dichloroethane at 293 K against DCJTB = 0.78 [12]. The HOMO energy levels were measured with low energy photo-electron spectrometry (Riken-Keiki AC-2). The thermal properties were measured by thermogravimetric analysis (TGA) (DSC7020) under N_2 at a heating rate of 10°C/min.

(1) 1,1,2,2,7,7-tetramethyljulolidine-9-carboaldehyde). Yield : 33.96% ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 9.87 (s, 1H), 7.53 (s, 1H), 7.48 (s, 1H), 3.42 (m, 2H), 3.31 (m, 2H), 1.82 (m, 2H), 1.41 (s, 6H), 1.38 (s, 6H), 1.09 (s, 6H); Mass (EI) $m/z = 285$ (M^+).

(2) 4-Dicyanomethylene-2-(1-pentylbicyclo-[2,2,2]oct-4-yl)-6-methyl-4H-pyran. Yield : 55.7% ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 5.31 (s, 1H), 5.20 (s, 1H), 1.77 (s, 3H), 1.52 (m, 6H), 1.31 (m, 6H), 1.18 (t, 2H, $J = 7.5$ Hz), 1.10 (m, 6H), 0.91 (t, 3H, $J = 7.5$ Hz); FT-IR (KBr): $\nu = 2925, 2323, 1587, 1520, 830$ cm^{-1}; Mass (EI) $m/z = 336$ (M^+).

(3) DCHMJPB. Yield : 29.6% ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.61 (s, 1H), 7.42 (s, 1H), 6.65 (d, 1H, $J = 12.1$ Hz), 6.43 (d, 1H, $J = 12.0$ Hz), 5.45 (s, 1H), 5.15 (s, 1H), 3.45 (m, 2H), 3.23 (m, 2H), 1.91 (m, 2H), 1.45 (m, 12H), 1.31 (m, 12H), 1.21 (s, 6H), 1.11 (t, 2H, $J = 7.5$ Hz), 1.02 (s, 6H), 0.91 (t, 3H, $J = 7.5$ Hz); FT-IR (KBr): $\nu = 2989, 2330, 1582, 1559, 1500$ cm^{-1}; Mass (EI) $m/z = 604$ (M^+); HRMS (EI) calcd for $C_{41}H_{53}N_3O$, 603.4189; found, 603.4178; mp. 258°C.

2.2. *Fabrication of OLED*

To prove the OLED characteristics, we fabricated EL devices with a device structure of ITO / *N*,*N*′-diphenyl-*N*,*N*′-(1-napthyl)-(1,1′-biphenyl)-4,4′-diamine (NPB) (40 nm) / tris(8-quionlinolato)-aluminium (Alq_3) : DCHMJPB (1, 2 or 3%) or DCJTB(1%) (20 nm) / Alq_3 (40 nm) / Liq (2 nm) / Al. After the fabrication, the current-voltage (J-V) characteristics of the OLEDs were measured with a source measure unit (Keithley 2400). The luminance and CIE chromaticity coordinates of the fabricated devices were measured using a chromameter (MINOLTA CS-100A). Electroluminance was measured using an Roper Scientific Pro 300i.

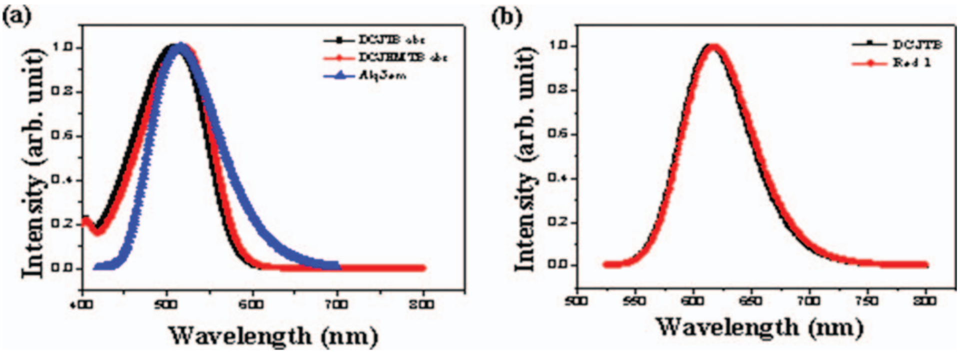


Figure 1. (a) UV-Vis spectra and (b) PL spectra of red emitters DCHMJPB and DCJTB.

Table 1. Physical properties of red emitters DCHMJPB and DCJTB.

Compound	$\lambda_{max}{}^{a}$ [nm]	$\lambda_{max}{}^{b}$ [nm]	FWHM [nm]	T_d [°C]	HOMO/ LUMO[eV]	E_g	Φ^c
DCHMJPB	520	619	71	387	−5.29/−3.13	2.16	0.81
DCJTB	511	619	72	270	−5.26/−3.10	2.16	0.78

[a]Maximum absorption and emission wavelength, measured in 1,2-dichloroethane solution [b]Obtained from AC-2 and absorption measurement. [c]Using DCJTB as a standard; $\lambda_{ex} = 500$ nm ($\Phi_p = 0.78$ in 1,2-dichloroethane)

3. Results and Discussion

The decomposition temperature (T_d) of DCHMJPB, defined as the temperature at which 5% mass loss occurs, was determined to be 387°C, which is higher than that of DCJTB 270°C [16]. This indicates that DCHMJPB is more stable than DCJTB. The UV-Vis absorption spectra of DCHMJPB and DCJTB are shown in Fig. 1(a). The maximum absorption peaks of these materials were 520 and 511 nm, respectively. Figure 1. (a) shows the good overlap between the emission spectra of Alq_3 and the absorption spectra of DCHMJPB and DCJTB. This observation imply that the Förster singlet energy transfer from host Alq_3 to red emitter DCHMJPB and DCJTB would be efficient. The emission λ_{mex} features of DCHMJPB and DCJTB were located at 619 nm and 619 nm, respectively, as shown in Figure 1. (b). The quantum yields of DCHMJPB and DCJTB were 0.81 and 0.78, respectively. The HOMO/LUMO levels for DCHMJPB and DCJTB were −5.29/-3.13 eV and -5.26/-3.10 eV, respectively. All physical properties were shown in Table 1.

All electroluminescent data on devices using DCHMJPB and DCJTB was summarized in Table 2.

Figure 2. shows the current density-voltage and the luminance-voltage characteristics of devices. The luminous and power efficiencies of devices are shown in Figure 3. The maximum luminous efficiency of devices 1 and 4 using DCHMJPB and DCJTB as dopants at the same dopping concentration were 4.20 and 2.52 cd/A, respectively. The luminous efficiency of devices 1 and 4 were 3.76 and 2.38 cd/A at 20 mA/cm^2, respectively. And the maximum power efficiency of devices 1 and 4 were 2.64 and 1.32 lm/W, respectively. The power efficiency of devices 1 and 4 were 1.97 and 1.06 cd/A at 20 mA/cm^2, respectively. Notably, compared to device 4 using DCJTB, the maximum luminous and power efficiency of device 1 using DCHMJPB increased by 67 and 100%, respectively, and the luminous

Table 2. EL performance characteristic of the doped-devices.

Device	Dopant[%]^a	L^b[cd/m^2]	LE$^{c/d}$[cd/A]	PE$^{c/d}$[lm/W]	EL[nm]	CIE^e(x' y)
1	DCHMJPB [1.0]	10960	4.20/3.76	2.64/1.97	608	(0.56, 0.42)
2	DCHMJPB [2.0]	5478	2.69/2.59	1.39/1.16	618	(0.60, 0.38)
3	DCHMJPB [3.0]	2363	1.36/1.23	0.71/0.51	620	(0.61, 0.38)
4	DCJTB [1.0]	6300	2.52/2.45	1.32/1.06	616	(0.60, 0.39)

[a]Dopping concentration. [b]Maximum luminance. [c]Maximum value. [d]At 20 mA/cm^2. [e]Commission Internationale d'Énclairage (CIE) coordinates at a 7.0 V.

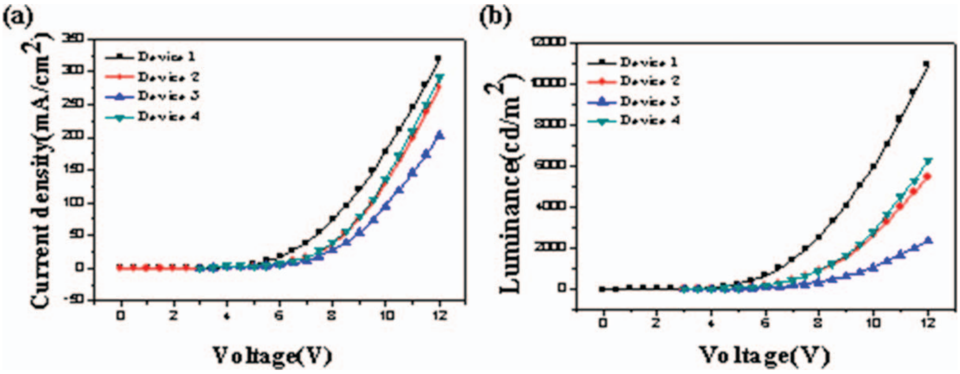


Figure 2. (a) Current density-voltage and (b) Luminance-voltage characteristics of devices 1–4.

and power efficiency of device 1 using DCHMJPB increased by 58 and 86% at 20 mA/cm^2, respectively. The additional methyl groups and 1-pentylbicyclo[2,2,2]octyl group of dopant DCHMJPB of device 1 could prevent molecular aggregation and thus reduce concentration quenching. This would contribute to the improved luminous efficiency of device 1 [17]. In addition, the other factor such as the higher quantum yield of DCHMJPB (0.81) than that of DCJTB (0.78) could contribute to the improved EL efficiencies of device 1 in comparison to device 4. In devices 1, 2 and 3 using DCHMJPB as a dopant at the different dopping concentrations, with the increase of doping concentration from 1% to 2 and 3%, the luminous and power efficiencies decreased due to the concentration quenching effect [18]. Figure 4. shows the EL spectra of devices 1–4. Interestingly, the EL spectra of device 1 showed Alq_3 emission around 510 nm due to the incomplete energy transfer from Alq_3 host to dopant DCHMJPB in the electron transporting layer. However, the EL spectra of devices 2 and 3 showed no Alq_3 emission due to the efficient exciton formation at dopant DCHMJPB with the increase of dopping concentrations. The CIE coordinates of device 1 is (0.56, 0.42) in the orange-red region. Interestingly, compared to device 1, device 2 and device 3 had the improved CIE coordinates of (0.60, 0.38) and (0.61, 0.38) at 7.0 V, approaching saturated red emission due to the excimer formation of DCHMJP.

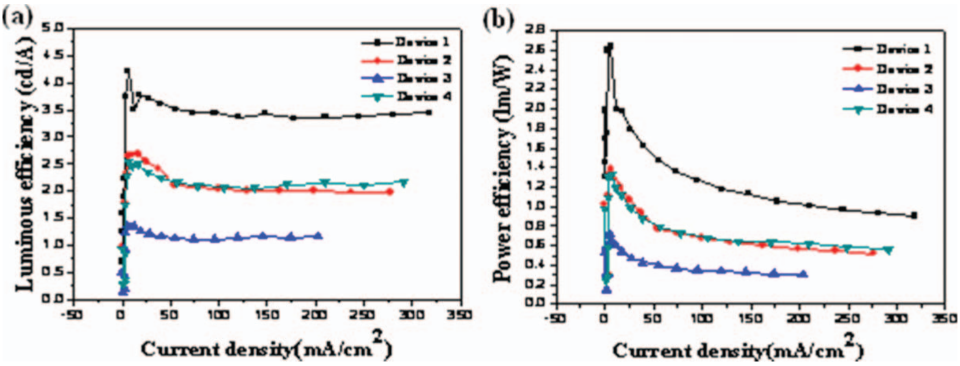


Figure 3. (a) Luminous efficiencies-current density and (b) Power efficiencies-current density characteristics of devices 1–4.

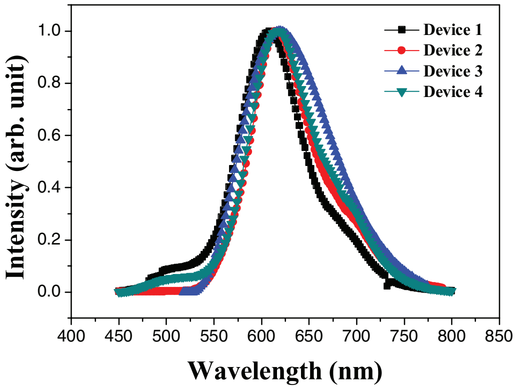


Figure 4. EL spectra the devices 1–4.

4. Conclusions

In summary, we have developed the efficient red electroluminescent DCHMJPB based on DCJTB derivative. Particularly, an device 1 using DCHMJP as a dopant exhibits the best performance with a maximum luminance of 10960 cd/m^2, and a luminous efficiency of 3.76 cd/A at 20 mA/cm^2. Also, this device shows orange-red emission with CIE coordinates of (0.56, 0.42) at 7.0V. Although an efficient orange-red OLED using DCHMJPB has insufficient color purity for applications to full-color displays, DCHMJPB can be used to fabricate efficient white organic light-emitting diodes (WOLEDs). Recently, highly efficient WOLEDs by a combination of fluorescent sky-blue and red emitters with complementary colors has been demonstrated [19]. Therefore, DCHMJPB is an excellent fluorescent red material for efficient WOLEDs with a combination of suitable sky blue emitters [20, 21].

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