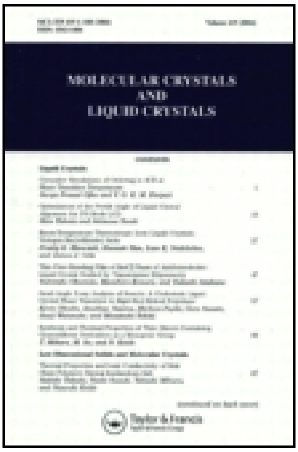

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An Efficient Red Organic Light-Emitting Diode Using DCJTB Type Emitters Based on Silicone-Containing Julolidine Derivatives

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An Efficient Red Organic Light-Emitting Diode Using DCJTB Type Emitters Based on Silicone-Containing Julolidine Derivatives

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*This paper reports the synthesis and electroluminescent properties of new red fluorescent materials, 4-(dicyanomethylene)-2-(1,1-dimethyl-7-trimethylsiliyl methyl-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJTMS**) and 4-(dicyanomethylene)-2-(1,7-bistrimethylsiliylmethyl-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJDTMS**). In these red emitters, the bulky groups such as trimethylsilane and n-pentyl-bicyclo[2,2,2]octane were introduced into and 4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)-styryl]-4H-pyran (DCM) skeleton to increase the steric hindrance between the red emitters and prevent concentration quenching. An OLED device using 4-(dicyanomethylene)-2-(1,7-bis(trimethylsiliylmethyl)-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJDTMS**) as a dopant exhibited the efficient red emission with a Luminous efficiency, Power efficiency and Commision Internationale De L'Eclairage ($CIE_{x,y}$) coordinates of 3.66 cd/A, 2.13 lm/W at 20 mA/cm^2 and (0.62, 0.38) at 7.0 V, respectively. Compared to device using 4-(dicyanomethylene)-2-(1,1,7,7-tetra-methyljulolidyl-9-enyl)-6-tert-butyl-4H-pyran (DCJTB), the red device using **DCJDTMS** showed the greatly improved EL efficiency due to the more bulky substituents of compound **DCJDTMS**.*

Keywords OLED; Red fluorescence; Trimethylsiliyl group; n-Pentyl-bicyclo[2,2,2]octane; DCJTB derivatives

Introduction

Since the first application of a multilayer structure in organic light-emitting diodes (OLEDs) by Tang and Vanslyke, OLEDs have attracted considerable attention owing to their easy processability, flexibility, thinness, low operating voltages, high resolution, wide viewing angles, and faster response time [1]. Therefore, OLEDs have become a technology for the next generation full color flat-panel displays. Many researchers have examined fluorescent and phosphorescent emitters for high device performance in OLEDs [2]. However, fluorescent red emitters are a limitation in realizing a full color display with low efficiency and satisfactory color purity [3].

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Up to now, a variety of red fluorescent emitters have been developed, including the push-pull red emitters based on arylamine-substituted polyaromatic hydrocarbon derivatives [4], polyacenes [5], metal chelates [6] and DCM derivatives [7]. Generally, red fluorescent emitters have electron donor-acceptor structures with a narrow band gap. In most cases, the concentration quenching due to excimer and exciplex formation reduce the EL performance dramatically. Therefore, there has been considerable effort in developing efficient red fluorescent materials by preventing excimer and exciplexes formation through the incorporation of sterically bulky moieties in the emitters. In particular, DCJTB was reported to show improved EL performance due to the introduction of a bulky tert-butyl group, which prevented concentration quenching [8]. However, their EL performance still requires improvement.

This paper describes the synthesis and electroluminescent properties of new red fluorescent materials, 4-(dicyanomethylene)-2-(1,1-dimethyl-7-trimethylsiliylmethyl-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJTMS**) and 4-(dicyanomethylene)- 2-(1,7-bis(trimethylsiliylmethyl)-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJDTMS**). In these red emitters, bulky groups, such as trimethylsilane and n-pentyl-bicyclo[2,2,2]octane, are introduced into the DCM skeleton to increase steric hindrance between red emitters and prevent concentration quenching. As will be demonstrated in below, a fluorescent red OLED using **DCJDTMS** exhibites efficient red emission with improved EL efficiency, compared to a device using DCJTB.

Experimental

Materials and Measurement

^{1}H- and ^{13}C- nuclear magnetic resonance (NMR) were recorded on a Varian (Unity Inova 300Nb) spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet Avatar 320 FT-IR spectrometer. The low- and high-resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in FAB mode, a Jeol JMS-600W spectrometer in EI mode and a JMS-T100TD (AccuTOF-TLC) in positive ion mode. The UV-Vis absorption and photoluminescence spectra of the newly designed red dopants were measured in a 10^{-5} M solution in 1,2-dichloroethane. The fluorescent quantum yields were determined in 1.2-dichloroethane at 293 K against DCJTB ($\Phi = 0.78$).[12] The HOMO energy levels were measured using a low energy photo-electron spectrometer (Riken-Keiki AC-2). The LUMO energy levels were estimated by subtracting the energy gap from the HOMO energy levels.

4-(dicyanomethylene)-2-(1,1-dimethyl-7-trimethylsiliylmethyl-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJTMS**). Piperidine (1.17 mmol) was added to a solution of compounds **1a** (0.26 mmol) and **2** (0.26 mmol) in anhydrous ethyl alcohol (10 ml) and heated to 140°C for 5 h with a dean-stark trap. After cooling in a refrigerator, the mixture was filtered with hexane and extracted with ethyl acetate and brine. After evaporating the solvent, the mixture was purified by silica column chromatography with ethyl acetate and hexane and re-crystallized with hexane. The obtained compound was a reddish solid (Yield : 70 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 7.25 (d, $J = 15.7$ Hz, 1H), 7.18 (d, $J = 1.9$ Hz, 1H), 7.06 (d, $J = 1.9$ Hz, 1H), 6.56 (d, $J = 2.1$ Hz, 1H), 6.41 (d, $J = 2.1$ Hz, 1H), 6.40 (d, $J = 15.7$ Hz, 1H), 3.45-3.36 (m, 1H), 3.32-3.18 (m, 3H), 2.96-2.91 (m, 1H), 1.88-1.73 (m, 10H), 1.54-1.49 (m, 6H), 1.33 (s, 3H), 1.30 (s, 3H), 1.26-1.17 (m, 8H), 0.96-0.93 (m, 2H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.09 (s, 9H); ^{13}C-NMR (75

MHz, $CDCl_3$): δ ppm 171.8, 161.0, 156.9, 143.1, 139.4, 130.2, 128.7, 126.0, 124.9, 121.3, 116.4, 116.3, 111.5, 105.2, 103.2, 56.6, 46.7, 41.5, 37.2, 36.1, 33.3, 32.9, 32.3, 30.8, 30.7, 30.6, 30.2, 30.0, 27.9, 25.0, 23.6, 22.9, 14.3, -0.30; FT-IR (KBr): $\nu = 2926$, 2861, 2204, 1640, 1597, 1540, 1419, 1319, 1304, 1176, 843 cm^{-1}; Mass (EI) *m/z* = 633 (M^+); HRMS (EI) calcd for $C_{41}H_{55}N_3OSi$, 633.4114; found,633.4107; mp: 234 °C.

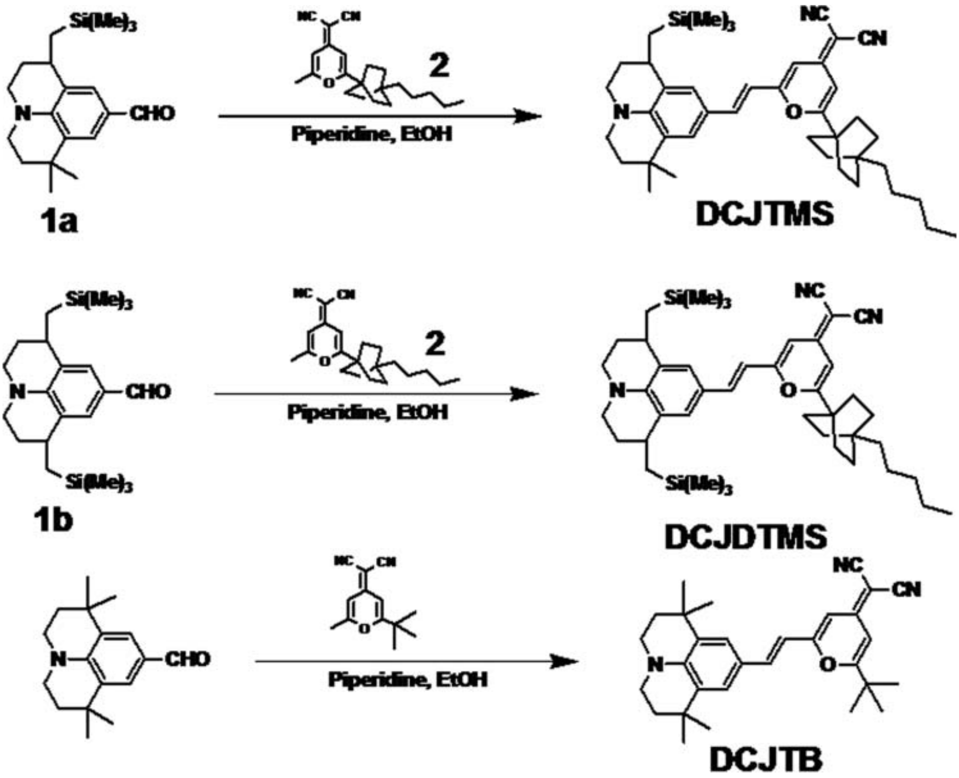
4-(dicyanomethylene)-2-(1,7-bis(trimethylsiliylmethyl)-julolidyl-9-enyl)-6-(4-pentylbicyclo[2.2.2]octan-1-yl)-4H-pyran (**DCJDTMS**). **DCJDTMS** was prepared using the method for synthesizing **DCJTMS** using compound **1b** instead of compound **1a**. The obtained compound was a reddish solid (Yield : 80 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 7.25 (d, *J* = 15.6 Hz, 1H), 7.02 (d, *J* = 4.7 Hz, 2H), 6.54 (d, *J* = 2.1 Hz, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 3.43-3.35 (m, 2H), 3.26-3.17 (m, 2H), 2.96-2.88 (m, 2H), 2.04-1.93 (m, 2H), 1.87-1.82 (m, 6H), 1.81-1.71 (m, 2H), 1.54-1.49 (m, 6H), 1.35-1.16 (m, 8H), 0.98-0.86 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.09 (s, 9H), 0.08 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ ppm 171.8, 161.0, 156.9, 143.5, 143.0, 139.4, 128.4, 128.3, 126.5, 121.2, 121.0, 116.5, 116.4, 111.4, 111.3, 105.1, 103.2, 56.5, 46.6, 46.1, 41.5, 37.2, 33.2, 33.1, 33.0, 30.8, 30.6, 30.0, 28.1, 27.9, 25.2, 23.6, 22.9, 14.3, −0.25, −0.30; FT-IR (KBr): $\nu = 2927$, 2858, 2204, 1640, 1594, 1542, 1492, 1423, 1312, 1161, 837 cm^{-1}; Mass (EI) *m/z* = 691 (M^+); HRMS (EI) calcd for $C_{43}H_{61}N_3OSi_2$, 691.4353; found, 691.4351; mp: 236 °C.

Results and Discussion

Scheme 1 shows the synthetic scheme of **DCJTMS, DCJDTMS** and DCJTB. The aldehyde intermediates were prepared using the known procedure [9]. Knoevenagel condensation of the corresponding aldehyde intermediates with the pyran intermediate **2** [9] provided red emitters **DCJTMS, DCJDTMS** and DCJTB in moderate yields. These compounds were fully characterized with ^{1}H- and ^{13}C-NMR, FTIR, and low- and high-resolution mass spectrometry.

Figure 1(a) presents the ultraviolet-visible (UV-Vis) absorption spectra of compounds **DCJTMS, DCJDTMS** and DCJTB. The maximum absorption peaks of compounds **DCJTMS, DCJDTMS** and DCJTB were 507, 504 and 513 nm, respectively. Figure 1(a) shows good overlap between the emission spectra of Alq_3 and the absorption spectra of compounds **DCJTMS, DCJDTMS** and DCJTB. The results suggest that Förster singlet energy transfer from Alq_3 to red emitters **DCJTMS, DCJDTMS** and DCJTB is efficient, and Alq_3 served well as a host in the OLEDs using these compounds as red dopant materials. Red emitters **DCJTMS, DCJDTMS** and DCJTB exhibited efficient red emission with maximum emission peaks of 621, 618 and 621 nm, respectively, as shown in Figure 1(b). The quantum yields of compounds **DCJTMS, DCJDTMS** and DCJTB were 0.49, 0.10 and 0.78, respectively [10]. Table 1 lists the physical properties.

To examine the electroluminescent properties of compound **DCJTMS** and **DCJDTMS**, multilayer OLED devices were fabricated with the following structure: Indium Tin Oxide (ITO)/ *N,N'*-diphenyl-*N,N'*-(2-napthyl)-(1,1'-phenyl)-4,4'-diamine(NPB) (400 Å)/Alq_3 (**DCJDTMS** 1 or 2 %, device A or B), (**DCJTMS** 1 %, device C), (DCJTB 1 %, device D) or (**DCJDTMS** 1 % with 30 % rubrene, device E) (200 Å) /tris-(8-quinolinolate) aluminium (Alq_3) (200 Å)/Liq (20 Å)/Al (1000 Å), respectively, as shown in Figure 2. NPB Alq_3 and Liq were used as the hole transporting layer, red host in the emitting layer as well as electron transporting layer (ETL), and electron injection layer, respectively. **DCJTMS,**



Scheme 1. Synthesis and structures of **DCJDTMS, DCJTMS**, and DCJTB.

DCJDTMS and DCJTB were used as red dopants in the emitting layer, respectively. Particularly, in device **E**, rubrene was used as cohost to improve the EL performances. Table 2 summarizes the electroluminescent data.

Figure 3 shows the EL efficiencies of devices **A-E**. The luminous and power efficiency of device **A** using **DCJDTMS** was 3.54 cd/A and 1.48 lm/W at 20 mA/cm^2, respectively. Compared to a device **C** and **D** using **DCJTMS** and DCJTB at the same doping concentration, a device **A** showed the improved EL efficiencies. For examples, compared to devices **C** and **D**, the luminous efficiency of device **A** increased by 134% and 49% and

Table 1. Physical properties of red emitters DCJTMS, DCJDTMS and DCJTB

compound	UV$_{max}$(nm)[a]	PL$_{max}$(nm)[a]	FWHM[b]	E$_g$[c]	Q.Y[d]	HOMO/LUMO[e]
DCJDTMS	504	618	83	2.20	0.10	−5.71/−3.51
DCJTMS	507	621	73	2.17	0.49	−5.44/−3.27
DCJTB	513	621	72	2.16	0.78	−5.26/−3.10

[a] Maximum absorption or emission wavelength in 1,2-dichloroethane (ca. 1 × 10^{-5} M). [b] The Full width at Half-Maximum peaks of Emission Spectra. [c] Energy band-gap [d] Using DCJTB as a standard; $\lambda_{ex} = 550$ nm ($\Phi = 0.78$ in 1,2-dichloroethene). [e] Obtained from AC-2 and absorption measurement.

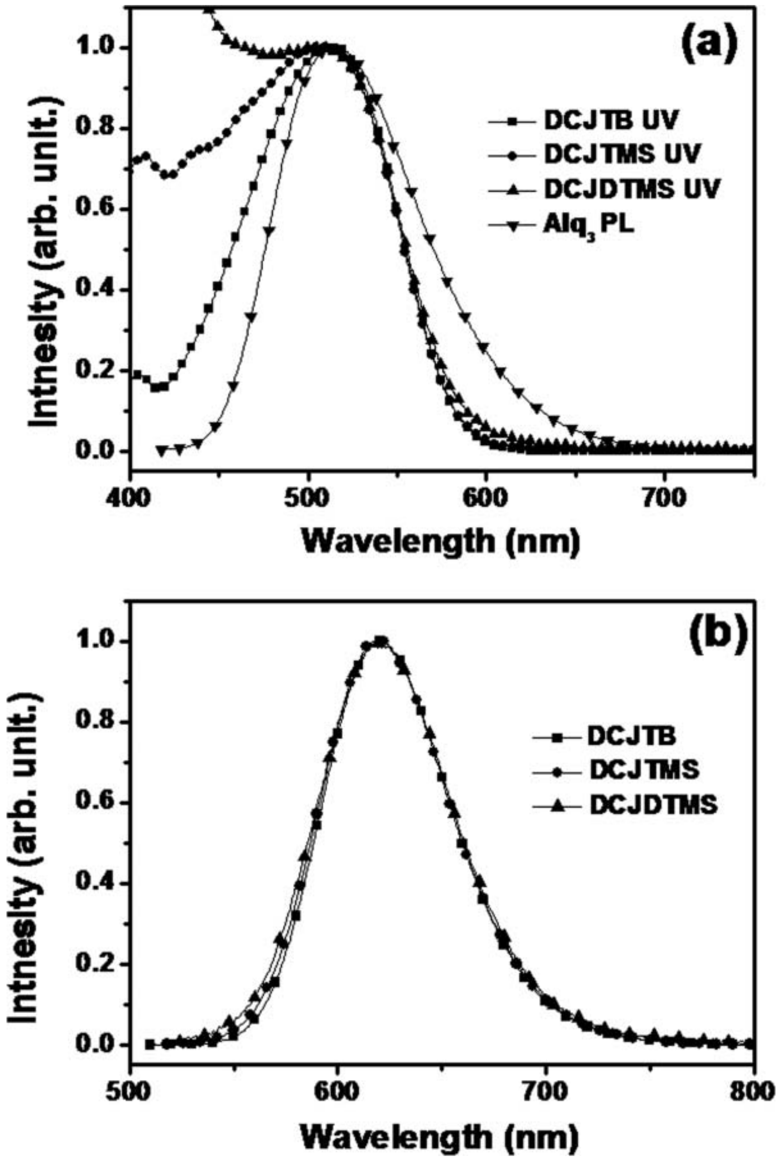


Figure 1. (a) UV-Vis absorption spectra and (b) PL spectra of **DCJDTMS, DCJTMS** and DCJTB.

the power efficiency of device **A** increased by 179% and 37% at 20 mA/cm^2, respectively. The bulky two trimethylsiliyl groups in compound **DCJDTMS** could partially contribute to the improved EL efficiency of device **A**. Presumably, the bulky groups of compound **DCJDTMS** in device **A** would increase the steric hindrance between red emitters in the emitting layer of the device **A** and lead to improve EL performance by preventing concentration quenching. In devices **A** and **B** using **DCJDTMS** as a dopant at the different dopping concentrations, with the increase of doping concentration from 1 % to 2 %, the luminous and power efficiencies decreased due to the concentration quenching effect.

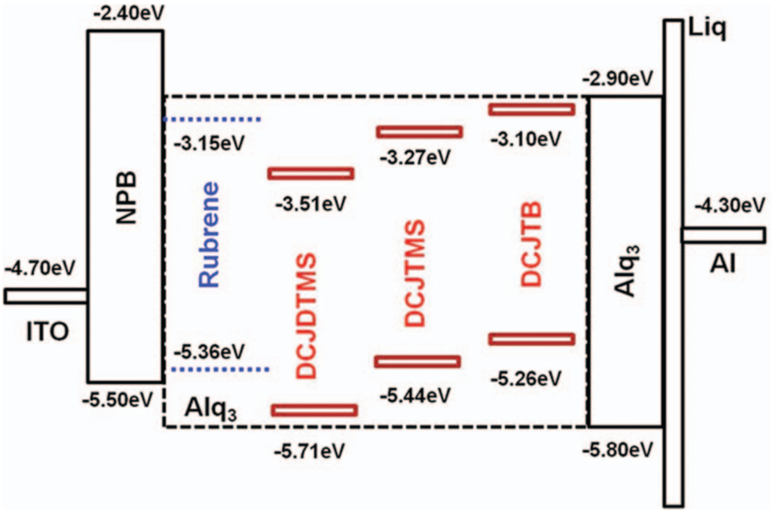


Figure 2. Structure and Energy-level diagram of devices.

Figure 4 shows the EL emission spectra of the red devices. The EL wavelengths of devices **A**–**E** were 608, 620, 616, 616, and 616 nm, respectively. The EL peaks of devices **A** and **B** showed increases in the intensities of the shoulder peaks due to the enhanced excimer formation under higher-doping conditions. The EL wavelengths of devices **A**, **C,** and **D** using different dopants at the same doping level were 608, 616, and 616 nm, respectively. The CIE coordinates of devices **A**, **C,** and **D** were (0.58, 0.42), (0.60, 0.39), and (0.60, 0.39) at 7.0 V, respectively. Device **A** showed smaller excimer peaks in the EL spectra than devices **C** and **D**, suggesting less excimer formation due to the bulky two trimethylsiliyl groups in the julolidine moiety of **DCJTMS** and **DCJTB**. Interestingly, there were shoulder peaks at approximately 510 nm in the EL spectra of devices **A, C,** and **D**, which might have originated from the green emission peak of Alq_3 host. This indicates incomplete energy transfer between host and dopant in the Alq_3 single-host emitting system.

The CIE coordinates of device **A** is (0.58, 0.42) in the orange-red region. Interestingly, compared to device **A**, device **E** using rubrene as a cohost had the improved CIE coordinates

Table 2. EL performance characteristic of devices A-E

Device	Dopant (doping %)	L [a] (cd/m^2)	LE-J [b] (cd/A)	PE-J[b] (lm/W)	EL[c] (nm)	CIE[c] (x,y)	V on[d] (V)
A	DCJDTMS (1%)	4880	3.54	1.48	608	(0.58, 0.42)	4
B	DCJDTMS (2%)	496	1.90	0.52	620	(0.62, 0.38)	4
C	DCJTMS (1%)	1410	1.51	0.53	616	(0.60, 0.39)	4
D	DCJTB (1 %)	6299	2.38	1.08	616	(0.60, 0.39)	3
E	DCJDTMS (1%) Rubrene (30%)	2380	3.66	2.13	616	(0.62, 0.38)	4

[a] Value at 12V. [b] The obtained value at 20 mA/cm^2, [c] The obtained value at 7.0 V. [d] Turn-on voltage at 1cd/m^2.

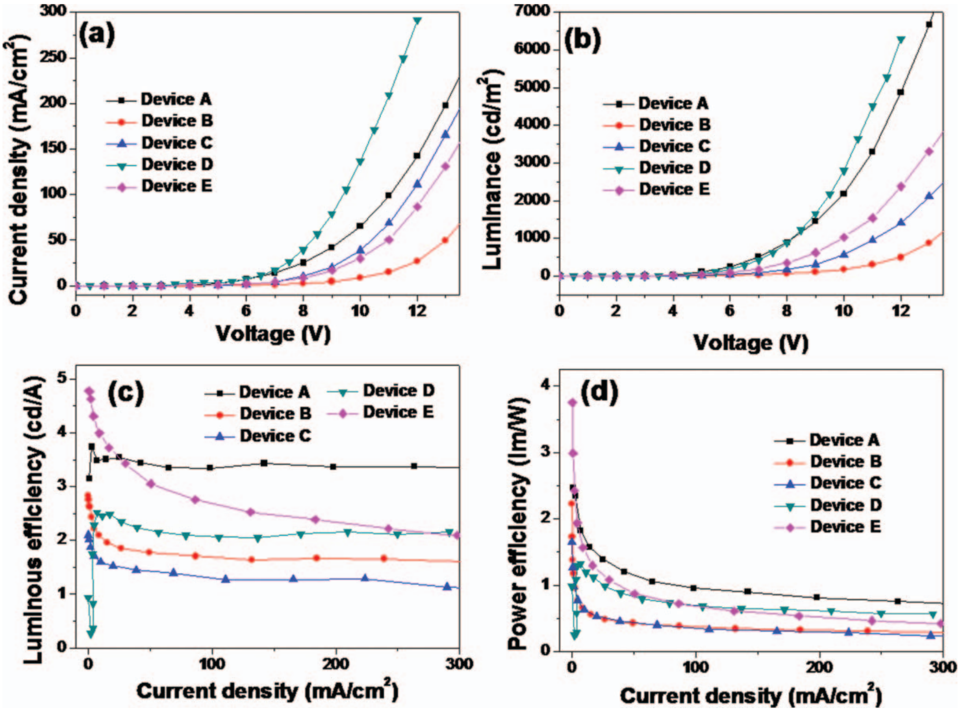


Figure 3. (a) *J-V*, (b) *L-V*, (c) *LE* versus current density, and (d) *PE* versus current density characteristics of devices **A-E.**

of (0.62, 0.38) at 7.0 V. Compared to EL spectra of device **A**, device **E** was not exhibited a Alq_3 emission, which shows that energy transfer between the host and dopant is more effective in the rubrene-Alq_3 co-host emitting system than the Alq_3 single-host emitting system [11]. These observations are imply that a cohost such as rubrene increase energy

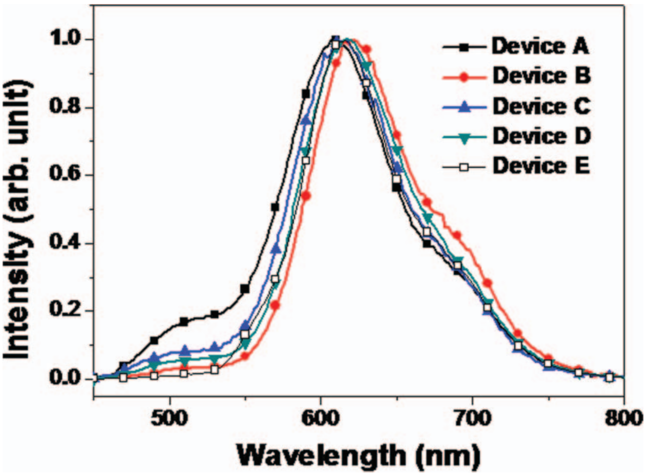


Figure 4. EL spectra of device **A-E.**

transfer efficiency from Alq_3 to **DCJDTMS** and thus improve the color purity. Furthermore, compared to device **A**, the luminous and power efficiencies of device **E** increased by 3.4% and 44% at 20 mA/cm^2, respectively. These phenomena give rise to the higher luminance efficiency and improved color purity. This study demonstrates that **DCJDTMS** with a modified julolidine moiety have excellent properties for use as red-emitting materials for OLEDs.

Conclusions

In conclusion, a red organic light-emitting diode using a new fluorescent red emitter **DCJDTMS** exhibited efficient red emission with a LE and PE of 3.66 cd/A and 2.13 lm/W at 20 mA/cm^2, respectively. The device showed the CIE$_{x,y}$ coordinates of (0.62, 0.38) at 7.0 V. Compared to the control device using DCJTB, the red device using **DCJDTMS** showed greatly improved EL efficiency due to the more bulky substituents in dopant **DCJDTMS** than those of DCJTB, Thus **DCJDTMS** is an excellent fluorescent red material for efficient OLEDs.

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