

## Red Fluorescent DCM Derivatives with the Bulky-substituents on Pyran and Julolidine Moieties for Organic Light-Emitting Diodes (OLEDs)

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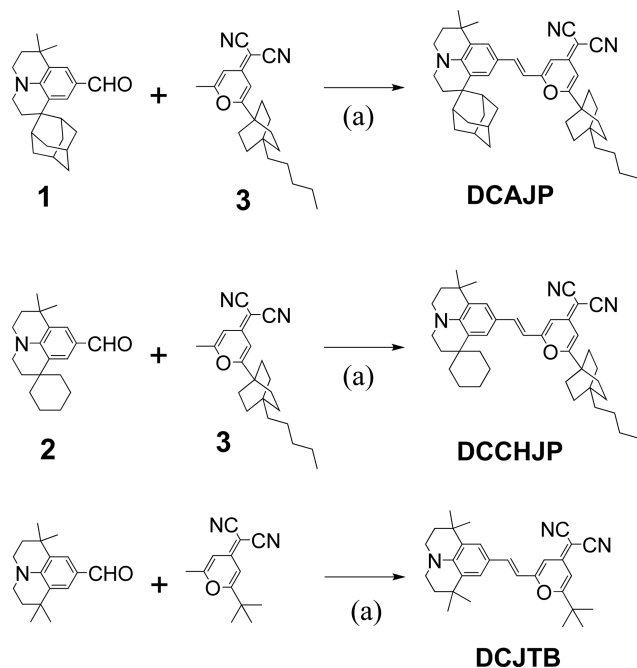
Organic light-emitting diodes (OLEDs) have received considerable attention due to their potential application in flat panel displays.<sup>1</sup> To develop three primary color-emitting materials for full color organic light-emitting diodes, there has been considerable effort to search for the efficient emitting materials.<sup>2</sup> Particularly, a variety of red fluorescent materials including the derivatives of 4-(dicyanomethylene)-2-methyl-6-*p*-(dimethylamino)styryl]-4*H*-pyran (DCM) have been widely studied, because red fluorescent emitting materials are far from ideal in terms of efficiency and color purity.<sup>3-10</sup> In most DCM type emitters, concentration quenching due to excimer and exciplex formation dramatically reduces EL performance. Among those, 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (**DCJT**) represents one of the most efficient fluorescent red emitting materials for OLEDs. In **DCJT**, the bulky substituents such as four methyl groups on julolidine moiety and *tert*-butyl group on pyran 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.<sup>11</sup> However, their EL performances still need to be improved.

In this paper, we describe the synthesis and electroluminescent properties of two red fluorescent DCM derivatives, 4-(dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1-dimethyl-7,7-adamantyljulolidyl-9-enyl)-4*H*-pyran (**DCAJP**) and 4-(dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1-dimethyl-7,7-cyclohexyljulolidyl-9-enyl)-4*H*-pyran (**DCCHJP**). In these red emitters, pyran moieties have the bulky 1-pentylbicyclo[2,2,2]octyl groups. Furthermore, compared to **DCJT**, two additional adamantyl group and cyclohexyl group are introduced on julolidine moieties of **DCAJP** and **DCCHJP**, respectively. These bulky groups would increase steric hindrance and prevent the self-aggregation between red emitters in the emitting layer of devices. Therefore, OLED devices using these emitting materials would have the improved EL performances by reducing concentration quenching.

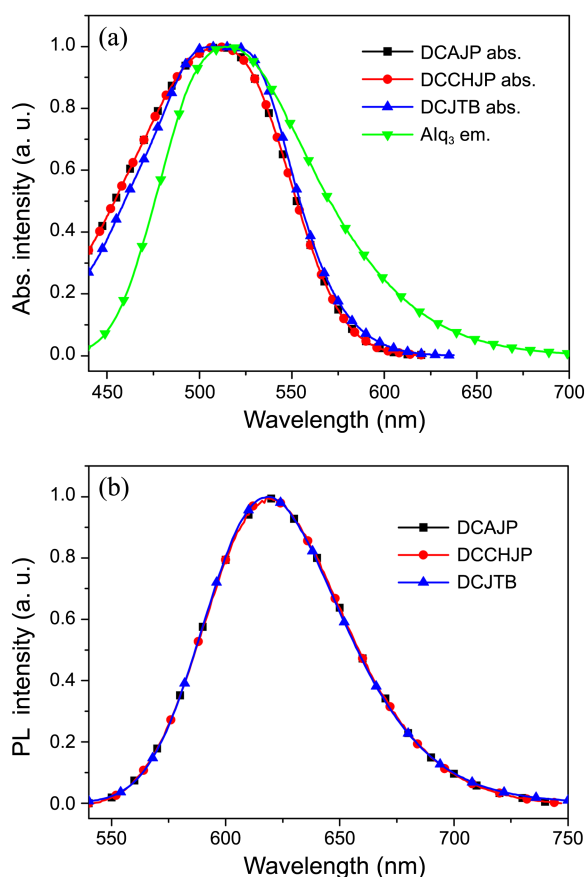
Structures and synthetic scheme of **DCAJP** and **DCCHJP** were shown in Scheme 1. Synthesis of these red emitters began with the preparation of 1,1-dimethyl-7,7-adamantyljulolidine-9-carboaldehyde, 1,1-dimethyl-7,7-cyclohexyljulolidine-9-carboaldehyde and 2-methyl-6-(1-pentylbicyclo

[2,2,2]oct-4-yl)-4-(dicyanomethylene)-4*H*-pyran by following the known procedure.<sup>12,13</sup> Subsequently, Knoevenagel condensation in the presence of piperidine provided the red emitter **DCAJP** and **DCCHJP** with the moderate yield. **DCJT** was prepared by following the standard procedure. These compounds were fully characterized with <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR, low- and high-resolution mass spectrometry.

The ultraviolet-visible (UV-Vis) absorption spectra of **DCAJP**, **DCCHJP** and **DCJT** are shown in Figure 1(a). The maximum absorption peaks of these materials were 511 nm, respectively. Figure 1(a) shows the good overlap between the emission spectra of a common fluorescent red host material Alq<sub>3</sub> and the absorption spectra of **DCAJP**, **DCCHJP** and **DCJT**. This observation imply that the Förster singlet energy transfer from host Alq<sub>3</sub> to red emitter **DCAJP**, **DCCHJP** and **DCJT** would be efficient, and Alq<sub>3</sub> served well as a host in the OLEDs by using these compounds as red dopant materials. Red emitters **DCAJP**, **DCCHJP** and **DCJT** exhibit efficient red emissions with



**Scheme 1.** Synthesis and structures of **DCAJP** and **DCCHJP**. (a) Piperidine, EtOH, 25 °C.



**Figure 1.** (a) UV-Vis spectra and (b) PL spectra of red emitters **DCAJP**, **DCCHJP** and **DCJTB**.

maximum emission peaks of 618, 618 and 619 nm, respectively, as shown in Figure 1(b). The quantum yields of **DCAJP**, **DCCHJP** and **DCJTB** were 0.88, 0.87 and 0.78, respectively. The HOMO/LUMO levels for **DCAJP**, **DCCHJP** and **DCJTB** were  $-5.33/-3.17$ ,  $-5.34/-3.18$  and  $-5.26/-3.10$  eV, respectively. All physical properties were shown in Table 1.

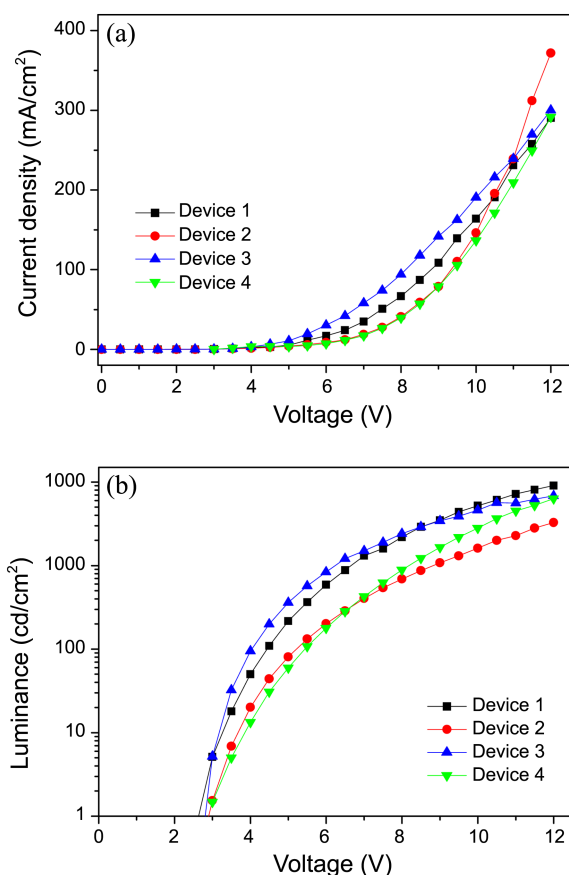
To explore the electroluminescent properties of **DCAJP** and **DCCHJP**, OLED devices using **DCAJP** and **DCCHJP** as dopants in **Alq<sub>3</sub>** host were fabricated. NPB, **Alq<sub>3</sub>**, and Liq were used for hole transporting layer, red host and electron transporting layer, and electron injection layer, respectively. Particularly, to optimize the device structure, two kinds of devices with the different doping concentrations such as 1% and 2% were fabricated. Also, for the comparison, the control device using **DCJTB** as a dopant in **Alq<sub>3</sub>** host at 1% doping concentration was fabricated. All electroluminescent data on devices using **DCAJP**, **DCCHJP** and **DCJTB** were 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 luminous efficiency of devices **1**, **3** and **4** using **DCAJP**, **DCCHJP** and **DCJTB** as dopants at the same doping concentration were 3.79, 2.94 and 2.45 cd/A at 20 mA/cm<sup>2</sup>, respectively. And the power efficiency of devices **1**, **3** and **4**

**Table 1.** Physical properties of red emitters **DCAJP**, **DCCHJP** and **DCJTB**

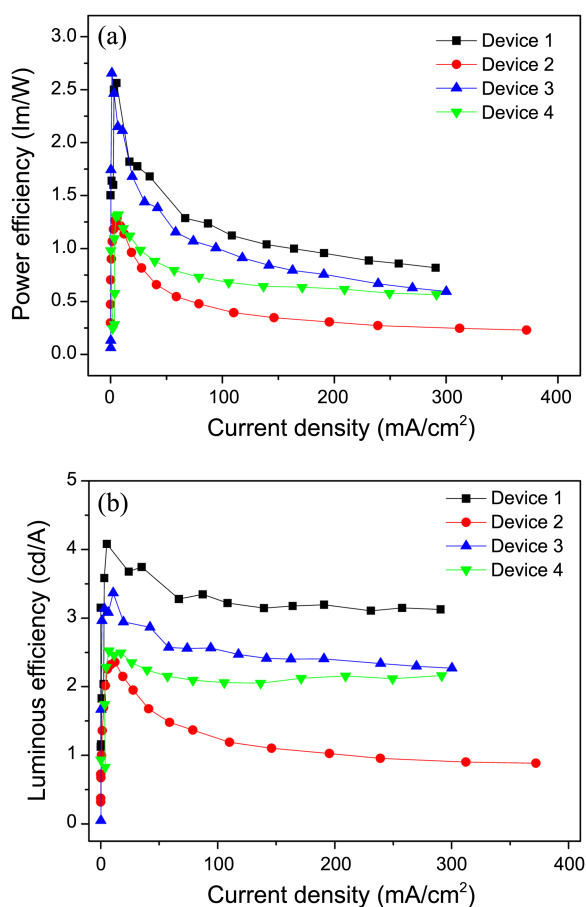
Compound	UV <sub>max</sub> <sup>a</sup> (nm)	PL <sub>max</sub> <sup>a</sup> (nm)	FWHM	HOMO/LUMO <sup>b</sup> (eV)	E <sub>g</sub>	Q.Y. <sup>c</sup>
<b>DCAJP</b>	511	618	72	$-5.33/-3.17$	2.16	0.88
<b>DCCHJP</b>	511	618	72	$-5.34/-3.18$	2.16	0.87
<b>DCJTB</b>	511	619	72	$-5.26/-3.10$	2.16	0.78

<sup>a</sup>Maximum absorption and emission wavelength, measured in 1,2-dichloroethane solution ( $1 \times 10^{-5}$  M). <sup>b</sup>Obtained from AC-2 and absorption measurement. <sup>c</sup>Using **DCJTB** as a standard;  $\lambda_{\text{ex}} = 500$  nm ( $\Phi_p = 0.78$  in 1,2-dichloroethane).<sup>11</sup>



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

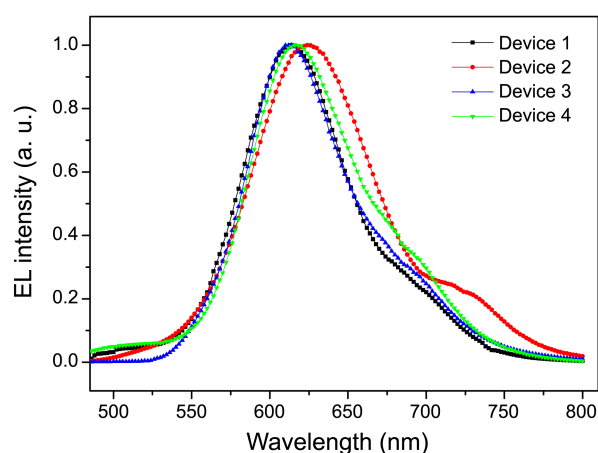
were 1.80, 1.66 and 1.08 cd/A at 20 mA/cm<sup>2</sup>, respectively. Notably, compared to device **4** using **DCJTB**, the luminous and power efficiency of device **1** using **DCAJP** increased by 55 and 67% at 20 mA/cm<sup>2</sup>, respectively. Also, the luminous and power efficiency of device **3** using **DCCHJP** increased by 20 and 54% at 20 mA/cm<sup>2</sup>, respectively, in comparison with device **4**. The additional adamantyl and 1-pentyl-bicyclo[2,2,2]octyl groups of dopant **DCAJP** of device **1** could prevent molecular aggregation and thus reduce concentration quenching. This would contribute to the improved luminous efficiency of device **1**. However, the other factor such as the higher quantum yield of **DCAJP** (0.88) than that of **DCJTB** (0.78) could contribute to the improved EL efficiencies of device **1** in comparison to device **4**.



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

In devices 1 and 2 using **DCAJP** as a dopant at the different doping concentrations, with the increase of doping concentration from 1% to 2%, the luminous and power efficiencies decreased due to the concentration quenching effect. Interestingly, the EL spectra of device 2 with the high doping concentration of **DCAJP** showed the shoulder peaks around 720 nm, which might be originated from the excimers of dopant **DCAJP** in the emitting layer.

Figure 4 shows the EL spectra of devices 1-4. Devices 1, 3 and 4 using **DCAJP**, **DCCHJP** and **DCJTB** as dopants at 1% doping concentration showed the efficient orange-red emission with the maximum emission peaks of 614, 614 and 616 nm, respectively, which were well compatible with the trend of PL spectra of **DCAJP**, **DCCHJP** and **DCJTB**. The CIE coordinates of devices 1, 3 and 4 were (0.59, 0.40), (0.60, 0.39) and (0.60, 0.39), respectively. Compared to



**Figure 4.** EL spectra the devices 1-4.

device 1, device 2 had the improved CIE coordinates of (0.62, 0.37) at 7.0 V, approaching saturated red emission due to the excimer formation of **DCAJP** due to the contribution of excimers of **DCJAP** at the high doping concentration. Although an efficient orange-red OLED using **DCAJP** has insufficient color purity for applications to full-color displays, **DCAJP** 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.<sup>14</sup> Therefore, **DCAJP** is an excellent fluorescent red material for efficient WOLEDs with a combination of suitable sky blue emitters.<sup>15</sup>

In conclusion, we designed and synthesized two red emitters 4-(dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1-dimethyl-7,7-adamantyljulolidyl-9-enyl)-4H-pyran (**DCAJP**) and 4-(dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1-dimethyl-7,7-cyclohexyljulolidyl-9-enyl)-4H-pyran (**DCCHJP**). A device with the structure of ITO/NPB (40 nm)/Alq<sub>3</sub>: **DCAJP** (1%) (20 nm)/Alq<sub>3</sub> (40 nm)/LiQ (2 nm)/Al showed the luminous and power efficiencies of 3.79 cd/A and 1.80 lm/W at 20 mA/cm<sup>2</sup>, respectively. The CIE coordinates of this device was (0.59, 0.40) at 7.0 V. Compared to a device using **DCJTB**, this device showed the improved EL performances due to reducing the molecular aggregation and thus preventing concentration quenching.

## Experimental Section

The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra

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

Device	Dopant [%] <sup>a</sup>	L <sup>b</sup> [cd/m <sup>2</sup> ]	V <sub>on</sub> <sup>c</sup> [V]	LE <sup>b,d,e</sup> [cd/A]	PE <sup>b,d,e</sup> [lm/W]	EL [nm]	CIE <sup>f</sup> (x, y)
1	<b>DCAJP</b> [1.0]	9085	2.6	4.08/3.79/3.71	2.56/1.80/1.89	614	(0.59,0.40)
2	<b>DCAJP</b> [2.0]	3280	2.9	2.36/2.12/1.97	1.29/0.94/0.84	624	(0.62,0.37)
3	<b>DCCHJP</b> [1.0]	6817	2.8	3.37/2.94/2.97	2.65/1.66/1.75	614	(0.60,0.39)
4	<b>DCJTB</b> [1.0]	6299	2.9	2.50/2.45/2.44	1.32/1.08/1.07	616	(0.60,0.39)

<sup>a</sup>Doping concentration. <sup>b</sup>Maximum luminance 12.0 V. <sup>c</sup>Turn-on voltage at 1.0 cd/m<sup>2</sup>. <sup>d</sup>Maximum value. <sup>e</sup>At 20 mA/cm<sup>2</sup>. <sup>f</sup>At 500 cd/m<sup>2</sup>. <sup>g</sup>Commission Internationale de l'Enclairage (CIE) coordinates at a 7.0 V.

were recorded on a Varian (Unity Inova 300Nb) spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded using a Boker VERTEX70 FT-IR spectra spectrometer. The low- and high-resolution mass spectra were measured using a JEOL JMS-600W spectrometer in Electron ionization (EI) mode. The ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra of these designed red dopants were measured in 1,2-dichloroethane at a concentration of  $10^{-5}$  M. The fluorescent quantum yield was determined in 1,2-dichloroethane at 293 K against DCJTB ( $\Phi = 0.78$ ).<sup>11</sup> The highest occupied molecular orbital (HOMO) energy level was measured by low-energy photoelectron spectrometry (Riken Keiki AC-2). The lowest unoccupied molecular orbital (LUMO) energy level was estimated by subtracting the energy gap from the HOMO energy level.

**Synthesis of DCAJP (4-(Dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1-dimethyl-7,7-adamantyl-julolidyl-9-enyl)-4H-pyran).** To a solution of 0.35 g of **1** (1.00 mmol) and 0.34 g of **3** (1.47 mmol) in 20 mL of EtOH was added 0.58 mL of piperidine (5.88 mmol) at room temperature. After refluxing under deanstark trap for 5 h, the resulting crude solid products was filtered and then washed with brine. Recrystallized with ethyl alcohol provided 0.21 g of DCAJP as reddish solids (0.315 mmol, 32%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d,  $J = 1.6$  Hz, 1H), 7.29 (d,  $J = 15.3$  Hz, 1H), 7.19 (d,  $J = 1.6$  Hz, 1H), 6.56 (d,  $J = 2.1$  Hz, 1H), 6.40 (d,  $J = 2.1$  Hz, 1H), 6.38 (d,  $J = 15.1$  Hz, 1H), 3.29-3.23 (m, 4H), 2.28 (s, 1H), 2.24 (s, 1H), 2.14 (s, 4H), 2.02-1.96 (m, 2H), 1.91-1.83 (m, 8H), 1.76-7.71 (m, 8H), 1.59-1.49 (m, 6H), 1.31 (s, 6H), 1.26-1.17 (m, 8H), 0.89 (t,  $J = 6.9$  Hz, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 165.1, 161.2, 156.9, 143.9, 140.0, 131.1, 131.0, 124.6, 124.5, 120.5, 116.6, 116.4, 111.1, 105.0, 103.2, 92.1, 56.3, 46.3, 46.0, 41.5, 41.3, 39.4, 37.2, 36.3, 35.1, 33.8, 33.0, 32.3, 32.1, 31.1, 30.8, 30.6, 30.3, 29.9, 28.3, 27.9, 23.6, 22.9, 14.3; FT-IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2909, 2360, 2203, 1637, 1536, 1490, 1462, 1180, 844; Mass (EI)  $m/z = 667$  (M<sup>+</sup>); HRMS (EI) calcd for C<sub>46</sub>H<sub>57</sub>N<sub>3</sub>O, 667.4502; found, 667.4497.

**Synthesis of DCCHJP (4-(Dicyanomethylene)-2-(1-pentylbicyclo[2,2,2]oct-4-yl)-6-(1,1-dimethyl-7,7-cyclohexyljulolidyl-9-enyl)-4H-pyran).** To a solution of 0.30 g of **2** (1.00 mmol) and 0.34 g of **3** (1.00 mmol) in 20 mL of EtOH was added 0.58 mL of piperidine (5.88 mmol) at room temperature. After refluxing under deanstark trap for 5 h, the resulting crude solid products was filtered and then washed with brine. Recrystallization with ethyl alcohol provided 0.27 g of DCCHJP as reddish solids (0.439 mmol, 44%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d,  $J = 1.8$  Hz, 1H), 7.27 (d,  $J = 15.8$  Hz, 1H), 7.23 (d,  $J = 1.8$  Hz, 1H), 6.58 (d,  $J = 2.0$  Hz, 1H), 6.44 (d,  $J = 15.2$  Hz, 1H), 6.41 (s, 1H), 3.29-3.22 (m, 4H), 1.90 (t,  $J = 6.0$  Hz, 2H), 1.88-1.83 (m, 6H), 1.79-1.83 (m, 10H), 1.55-1.52 (m, 8H), 1.49-1.32 (m, 8H), 1.26-1.18 (m, 6H), 0.89 (t,  $J = 6.9$  Hz, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 161.0, 156.9, 143.7, 139.5, 131.6, 130.5, 124.4, 124.0, 121.3, 116.4, 115.5, 111.7, 105.2, 103.2,

92.4, 56.6, 46.9, 46.8, 41.5, 37.4, 37.2, 36.2, 35.5, 33.0, 32.4, 30.8, 30.7, 30.6, 30.0, 28.2, 26.3, 23.6, 22.9, 21.8, 14.3; FT-IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2922, 2360, 2205, 1637, 1597, 1538, 1487, 1315, 1184, 843; Mass (EI)  $m/z = 615$  (M<sup>+</sup>); HRMS (EI) calcd for C<sub>42</sub>H<sub>53</sub>N<sub>3</sub>O, 615.4189; found, 615.4183.

**Device Fabrication and Characterization.** OLEDs using red-light-emitting molecules were fabricated by vacuum ( $10^{-6}$  torr) thermal evaporation onto pre-cleaned ITO coated glass substrates. All processes were carefully produced. The indium tin oxide (ITO) was first cleaned with acetone, methyl alcohol, distilled water, and kept in isopropyl alcohol for 48 h and dried by N<sub>2</sub> gas. The device structures were as follows: (1) ITO/N,N'-diphenyl-N,N'-(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) (40 nm)/tris(8-quinolinolato)-aluminium (Alq<sub>3</sub>): Red dopant (1 or 2%) (20 nm)/Alq<sub>3</sub> (40 nm)/LiQ (2 nm)/Al. All of the properties of the OLEDs such as the current density ( $J$ ), luminance ( $L$ ), luminance efficiency (LE), power efficiency (PE), and commission international de l'Éclairage (CIE) coordinate characteristics were measured using a Keithly 2400 source measurement unit and a Chroma meter MINOLTA CS-1000A. Electroluminescence was measured using a Roper Scientific Pro 300i.

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