Highly Efficient Red Organic Light-Emitting Diodes Using Methylcyclohexylpyran-Containing Emitters

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Since the pioneering work on organic light-emitting devices (OLEDs) by Tang and VanSlyke,[1] OLEDs have attracted considerable attention for their promising applications in high-efficiency, low-drive-voltage, large-area, full-color thin flat-panel displays and white lighting devices. To display full-color, blue-, green-, and red-light-emitting materials are required, and one of the major challenges for OLED research is to develop red-light fluorescent emitters with high luminous efficiency and ideal color purity.[2-7] On the other hand, it is difficult to develop new red fluorescent emitters with excellent electroluminescence properties and a saturated red color because of the significant concentration quenching by the self aggregation in most fluorescent red emitters.[8,9] Therefore, considerable efforts have been made to develop efficient red fluorescent materials by preventing concentration quenching through the incorporation of sterically bulky moiety in the emitters. A number of red fluorescent dyes have been synthesized but 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7,-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) is still the most efficient and studied.[10] In these materials, *tert*-butyl groups on pyran moiety have large steric hindrance due to its non-coplanar configuration, leading to a decrease in the molecular aggregation in the solid state. This helps improve the efficiency of red fluorescent OLED by reducing concentration quenching in the solid state. On the other hand, red fluorescent emitters require further improvement in terms of the efficiency, lifetime and color chromaticity.

In this paper, two methylcyclohexylpyran-containing electron donor-π-bridge-electron acceptor structures, 4-(dicyanomethylene)-2-(1-methylcyclohexyl)-6-(1,1,7,7-tetramethyljulolidyl)vinyl-4H-pyran (**DCJMC**) and 4-(2-methylene-1,3-indanedione)-2-(1-methylcyclohexyl)-6-(1,1,7,7-tetrametyljulolidyl)vinyl-4H-pyran (**IDJMC**), were synthesized and their electroluminescent properties were examined. In the pyran moieties of **DCJMC** and **IDJMC**, the bulky 1-methylcyclohexyl groups were incorporated in the DCJTB skeleton to increase the steric hindrance between the red emitters in the emitting layer of the devices and improve the EL performance by reducing molecular aggregation. In this study, tris-(8-hydroxyquinoline)aluminum (Alq3) is utilized as a host because it shows excellent stability and carrier transporting abilities and thus makes it generally a good host for red OLEDs. However, due to the incomplete energy

transfer between host and dopant, Alq3 has difficulty to realize pure and highly efficient red emissions. In order to prevent this problem, an assistant dopant such as rubrene is employed.[11,12] According to Hamada *et al.* applying rubrene to make the energy transfer easier from Alq3 to the red dopant [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H, 5H-benzo [ij] quinolizin-9-yl)-ethenyl]-4H-pyran4-ylidene] propane-dinitrile (DCM2) could improve color purity and efficiency of emission.[13] For this reason, it is expected that using rubrene enhance the energy transfer efficiency from Alq3 to the dopants and inproved the EL performance.

Scheme 1 outlines the synthesis of **DCJMC** and **IDJMC**. **DCJMC** and **IDJMC** were prepared by the Knoevenagel condensation of 1,1,7,7-tetramethyljulolidinylaldehyde with the corresponding active methylene compounds (**1a** and **2a**).[14] After conventional purification, such as column chromatography and recrystallization, these newly synthesized red-emitting materials (**DCJMC** and **IDJMC**) were purified by train sublimation under reduced pressure (< 10^{-3} Torr) and were fully characterized by ^{1}H- and ^{13}C-NMR, infrared (IR), and low- and high-resolution mass spectrometry.

Figure 1 shows the ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra of red dopant materials **DCJMC** and **IDJMC**. The maximum absorption peaks of **DCJMC** and **IDJMC** were 509 nm and 542 nm, respectively. The emission maxima of **DCJMC** and **IDJMC** appeared at 614 and 654 nm, respectively, in the red region of the visible spectrum. Compared to **DCJMC**, the absorption
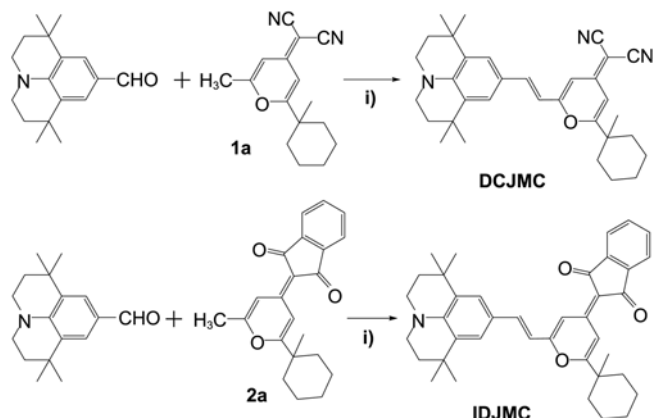
Scheme 1. Synthesis of **DCJMC** and **IDJMC**. i) Piperidine, EtOH.
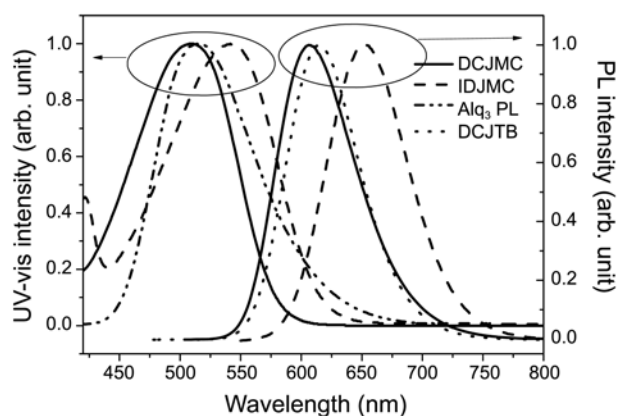
Figure 1. UV-vis absorption spectra and photoluminescence spectra of **DCJMC** and **IDJMC**.
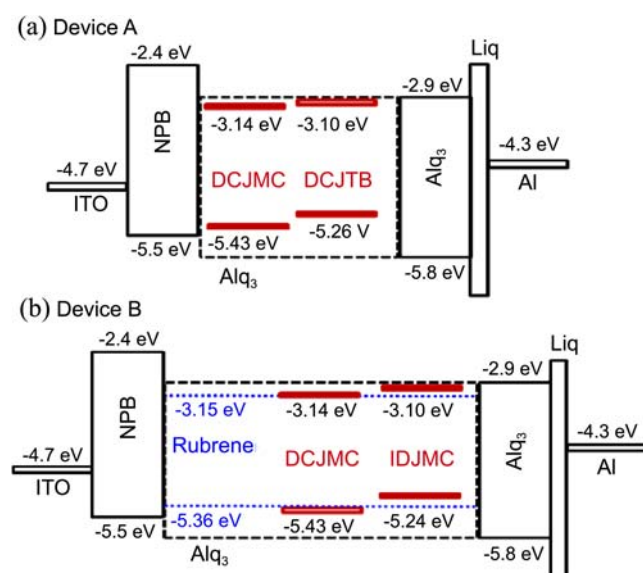
Figure 2. Energy-level diagram of OLEDs.

and emission spectrum of **IDJMC** showed bathochromic shifts due to the more extended -conjugation of the 1,3-indandione group than dicyanomethylene. The PL quantum yields of **DCJMC** and **IDJMC**, which were measured in 1,2-dichloroethane using DCJTB as the standard, were 0.87 and 0.55, respectively. The fluorescent quantum yield of **DCJMC** was higher than DCJTB, suggesting that these materials will have highly efficient electroluminescent properties in OLED devices.

The highest occupied molecular orbital (HOMO) level

was measured using a photoelectron spectrometer (Riken-Keiki AC-2) and the lowest occupied molecular orbital (LUMO) level was calculated by the optical band gap energy and HOMO level. The HOMO and LUMO energy levels were calculated to be −5.43 and −3.14 eV for **DCJMC** and −5.24 and −3.10 eV for **IDJMC**, respectively.

Figure 2 presents the device structure and HOMO/LUMO energy levels of the materials in the device. NPB was introduced as a hole-transporting layer to enhance hole injection and transport, Alq_3 functioned as an emitting layer as well as electron-transporting layer, whereas rubrene served as an assistant host.

Red devices **A** with the structure, ITO/NPB (40 nm)/ Alq_3: red dopant (x %) (20 nm)/ Alq_3 (40 nm)/ Liq (2 nm)/ Al, were fabricated to examine the electroluminescence (EL) properties of the dopant materials. The doping concentration of **DCJMC** was 0.6 wt % and 2.0 wt % to determine the optimized concentration. Figure 3 shows the current density-voltage-luminance characteristics (*J-L-V*) of the red devices. The luminous efficiencies of devices **A1**, **A2**, and **A3** were 3.99, 3.14, and 3.45 cd/A, respectively, at 20 mA/cm². The luminous efficiency decreased with increasing percentage of dopant due to the concentration-quenching effect. Therefore, the use of 0.6 wt % **DCJMC** provided an optimized doped device. In particular, compared to device **A3** using DCJTB as a dopant, the luminous efficiency and power of device **A1** using **DCJMC** as a dopant increased by 26% and 18%, respectively, at 20 mA/cm². Compared to DCJTB in device **A3**, the bulky 1-methylcyclohexyl group in the pyran moiety of **DCJMC** in device **A1** would prevent molecular aggregation between the emitter and thus improve the EL efficiency of a device using **DCJMC** as a dopant. In addition, the higher fluorescence quantum yield of **DCJMC** compared to DCJTB would partially contribute to the improved EL efficiencies of device **A1**.

Interestingly, the performance of the **DCJMC**-based electroluminescent device can be improved dramatically by co-doping, as shown in Figure 3-5 and Table 2. Device **B1**, which has the configuration, ITO/NPB (40 nm)/Alq_3: rubrene (30%): **DCJMC** (0.6%) (20 nm)/Alq_3 (40 nm)/Liq (2 nm)/Al (100 nm), was fabricated with the Alq_3 emissive layer co-doped with rubrene. Compared to device **A1**, the co-doping of rubrene with Alq_3 resulted in a decrease in the turn-on voltage from 4.0 to 2.5 V, an increase in luminous efficiency from 3.90 to 8.84 cd/A at 20 mA/cm², an enhancement in the power efficiency from 1.88 to 3.47

Table 1. Physical properties of red dopants **DCJMC**, **IDJMC** and **DCJTB**

Compound	UV_{max}[a] (nm)	PL_{max}[a] (nm)	FWHM	HOMO/LUMO[b] (eV)	E_g	Q.Y[c]	mp (°C)
DCJMC	509	614	76	−5.43/−3.14	2.29	0.87	255
IDJMC	542	654	78	−5.24/−3.10	2.14	0.55	221
DCJTB	511	620	72	−5.26/−3.10	2.16	0.78	

[a,b]Maximum absorption or emission wavelength in 1,2-dichloroethane (1×10^{-5} M). [b]Obtained from AC-2 and UV-vis absorption measurements. [c]Using DCJTB as a standard; λ_{ex} = 550 nm (Φ = 0.78 in 1,2-dichloroethene).
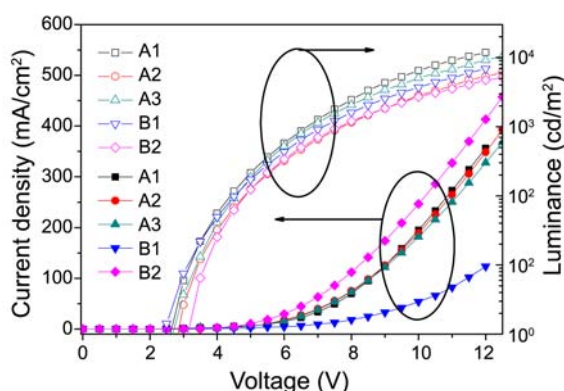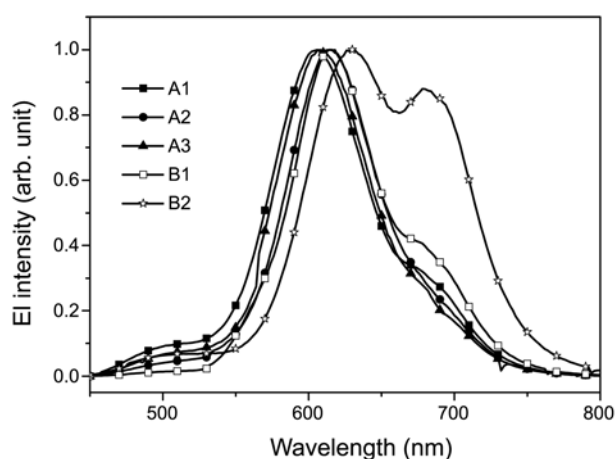
Figure 3. Current density-voltage-luminance (*J-V-L*) characteristics of the red devices.
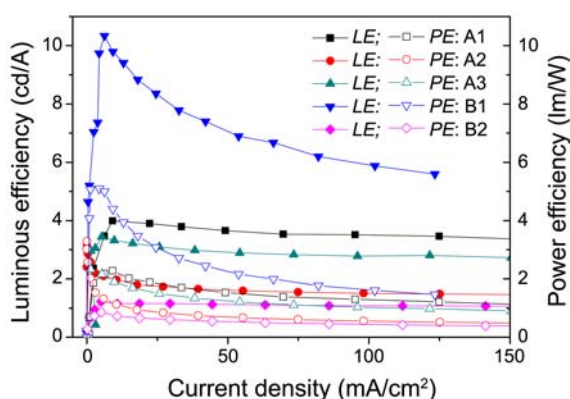
Figure 4. Luminous efficiency (*LE*) and power efficiency (*PE*)-current density characteristics of the red devices.

Figure 5. EL spectra of the red devices.

due to molecular aggregation between **IDJMC**.

The extended π-conjugated aromatic surface of **IDJMC** might facilitate molecular aggregation between **IDJMC** and reduce the EL efficiency of device **B2** using **IDJMC** as the dopant by concentration quenching compared to device **B1** using **DCJMC** as the dopant.

In conclusion, two novel red fluorescent materials (**DCJMC** and **IDJMC**) were designed and synthesized using 1,1,7,7-tetrametyljulolidine as an electron-donor group and methyl-cyclohexylpyran group as electron-acceptor groups on the DCJTB skeleton. Compared to the control device **A3** using DCJTB as a dopant, the luminous efficiency and power of device **A1** using **DCJMC** as a dopant increased by 26% and 18%, respectively, at 20 mA/cm^2. To further improve the EL performances, red OLEDs were fabricated, in which Alq$_3$ and rubrene were used as a co-host and the red fluorescent materials **DCJMC** and **IDJMC** as dopants. Compared to device **A1** using **DCJMC** as a dopant in Alq$_3$ single-host, the luminous and power efficiencies of device **B1** using the same dopant in Alq$_3$/rubrene co-host greatly increased by 127 and 84.6%, respectively, at 20 mA/cm^2. In addition, the change in the single-host to the co-host emitting system improves the CIE coordinates of the device from (0.57, 0.42) to (0.60, 0.40). Effective energy transfer between the host and dopant would contribute the improved EL performance in the co-host emitting system. Compared to the **DCJMC**-doped device, a device using **IDJMC** as a dopant showed improved CIE coordinates due to the extended -conjugation

lm/W at 20 mA/cm^2, and a shift in the CIE coordinates, from (0.57, 0.42) to (0.60, 0.40). Compared to device **A1**, a small shoulder peak of Alq$_3$ emission at approximately 510 nm were not observed in the EL spectrum of device **B1**, 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. This would lead to improved EL performance of the device **B1** compared to device **A1**. Compared to device **B1**, the EL spectra of device **B2** showed a bathochromic shift of 16 nm due to the more extended π-conjugation of 1,3-indandione group than di-cyanomethylene. Interestingly, the EL spectra of device **B2** exhibited an obvious excimer peak at approximately 690 nm

Table 2. EL performance characteristic of red OLEDs

Device	Dopant (doping %)	L^a (cd/m^2)	V$_{on}$^{b} (V)	LE^{c,d} (cd/A)	PE^{c,d} (lm/W)	EL^e (nm)	FWHM	CIE^e (x, y)
A1^f	**DCJMC**(0.6%)	11850	4.0	3.90/3.99	1.88/2.28	606	(0.57,0.42)	**A1**^{f}
A2^f	**DCJMC**(2.0%)	5298	4.0	1.79/3.14	0.90/3.29	614	(0.62,0.37)	**A2**^{f}
A3^f	**DCJTB**(0.6%)	9198	3.0	3.11/3.45	1.59/2.32	608	(0.58,0.40)	**A3**^{f}
B1^g	**DCJMC**(0.6%)	6903	2.5	8.84/10.34	3.47/5.10	614	(0.60,0.40)	**B1**^{g}
B2^g	**IDJMC**(0.6%)	4726	3.5	1.15/1.23	0.66/0.86	630/678	(0.63,0.36)	**B2**^{g}

^{a}Value of luminance at 12.0 V. ^{b}Turn-on voltage at 1.0 cd/m^2. ^{c}The measured at 20 mA/cm^2. ^{d}Maximum values. ^{e}Value measured at 7.0 V. ^{f}Device A: ITO/NPB (40 nm)/Alq3: red (x %) (20 nm)/Alq3 (40 nm)/Liq (2 nm)/Al. ^{g}Device B: ITO/NPB (40 nm)/Alq3: Rubrene (30%): red (x %) (20 nm)/Alq3 (40 nm)/Liq (2 nm)/Al.

by 1,3-indanedione. On the other hand, the EL efficiencies of this device decreased greatly due to molecular aggregation between **IDJMC** and concentration quenching.

Experimental Section

Materials and Measurement. ^{1}H- NMR and ^{13}C-NMR were recorded on a Varian (Unity Inova 300Nb) spectrometer. The FT-IR spectra were recorded using a Buuker VERTEX70 FT-IR spectrometer. Low-resolution mass 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 fluorescent quantum yields were determined in 1.2-dichloroethane at 293 K against DCJTB ($\Phi = 0.78$).[5,13]

4-(Dicyanomethylene)-2-(1-methylcyclohexyl)-6-(1,1,7,7-tetrametyljulolidyl)vinyl-4*H*-pyran (DCJMC): 1,1,7,7-tetramethyljulolidinylaldehyde (0.97 mmol) and **1a** (1.07 mmol) into RBF were added and connected to a deanstark trap (put the molecular sieve), reflux condenser. Anhydrous ethyl alcohol (12 mL) and piperidine (9.71 mmol) were added, heated to 110 °C for 8 h and then cooled in a refrigerator. The mixture was filtered and extracted with ethyl acetate and distilled water. After filtration and solvent evaporation, the mixture was purified by recrystallization with MC and hexane. The obtained compound was red solid (Yield: 83%).

^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.28 (d, $J = 15.7$ Hz 1H), 7.22 (s, 2H), 6.60 (d, $J = 1.8$ Hz, 1H), 6.52 (d, $J = 1.8$ Hz, 1H), 6.44 (d, $J = 15.4$ Hz, 1H), 3.03 (t, $J = 6.0$ Hz, 4H), 2.00-1.93 (m, 2H), 1.76 (t, $J = 6.0$ Hz, 4H), 1.62-1.50 (m, 8H), 1.32 (s, 15H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ (ppm): 171.7, 161.2, 157.0, 143.1, 139.6, 130.5, 124.4, 121.2, 116.4, 116.3, 111.6, 105.1, 103.8, 55.8, 46.9, 40.4, 36.1, 35.7, 32.4, 30.6, 26.5, 26.0, 22.4, FT-IR (ATR): ν (cm^{-1}) : 2360, 1635, 1596, 1542, 1539, 1181, 668; MS (EI$^+$) (*m/z*): 493 [M$^+$]; HRMS (TOF$^+$): [M$^+$+H] calculated for C$_{33}$H$_{40}$N$_3$O, 494.3171, found: 494.3165; mp 255 °C.

4-(2-Methylene-1,3-indanedione)-2-(1-methylcyclohexyl)-6-(1,1,7,7-tetrametyljulolidyl)vinyl-4*H*-pyran (IDJMC). Compound **IDJMC** was prepared by the method used to synthesize **DCJMC** using compound **1a** instead of **2a**. The obtained compound was a red solid (Yield: 78%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 8.46 (s, 1H), 8.42 (s, 1H), 7.76-7.71 (m, 2H), 7.60-7.56 (m, 4H), 7.32 (d, $J = 15.8$ Hz, 1H), 6.64 (d, $J = 15.7$ Hz, 1H), 3.29 (t, $J = 5.9$ Hz, 4H), 2.12-2.09 (m, 2H), 1.77 (t, $J = 6.0$ Hz, 4H), 1.68-1.60 (m, 8H), 1.36 (s, 3H), 1.34 (s, 12H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ (ppm): 166.2, 164.2, 163.2, 161.6, 158.0, 146.0, 144.1, 138.3, 133.0, 130.5, 124.3, 122.5, 121.2, 111.2, 107.4, 47.0, 44.9, 36.3, 36.0, 32.4, 30.7, 22.6, 18.8, 16.2, 0.2; FT-IR

(ATR): ν (cm^{-1}) :1494, 1473, 1461, 1418, 1403, 1317, 1228, 734; MS (EI$^+$) (*m/z*): 611 [M$^+$]; HRMS (TOF$^+$): [M$^+$+H] calculated for C$_{39}$H$_{44}$NO, 574.3321, found: 574.3317; mp 221 °C.

Device Fabrication and Characterization. Indium tin oxide (ITO) was washed with acetone, methyl alcohol, distilled water, and kept in isopropyl alcohol for 48 h and dried by N$_2$ gas. The structure of the OLEDs was as follows: ITO/*N*,*N*′-diphenyl-*N*,*N*′-(1-napthyl)-(1,1'-phenyl)-4,4'-diamine (NPB) (40 nm)/tris(8-quinolinolato)-aluminium (Alq$_3$): dopants **DCJMC** and DCJTB (20 nm, x%)/Alq$_3$ (40 nm)/ lithium quinolate (Liq) (2 nm)/Al (device A); ITO/NPB (40 nm)/Alq$_3$: **DCJMC** and **IDJMC** (0.6%): rubrene (30%, 20 nm)/Alq$_3$ (40 nm)/Liq (2 nm)/Al (device B). All the properties of the OLEDs, such as current density, luminance, luminous efficiency, and Commission Internationale de l'Eclairage coordinates (CIE) coordinate characteristics were measured using a Keithley 2400 source measurement unit and a Minolta CS-1000A Chroma Meter. EL was measured using a Roper Scientific Pro 300i spectrograph.

References and Notes

1. Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
2. Lee, K. H.; Kim, S. M.; Kim, J. Y.; Kim, Y. K.; Yoon, S. S. *Bull. Korean. Chem. Soc.* **2010**, *31*, 2884.
3. Lee, K. H.; Park, M. H.; Kim, J. Y.; Kim, S. M.; Seo, B. M.; Seo, J. H.; Kim, Y. K.; Yoon, S. S. *J. Nanosci. Nanotechnol*. **2011**, *11*, 1484.
4. Lee, K. H.; Park, M. H.; Kim, S. M.; Kim, Y. K.; Yoon, S. S. *Jpn. J. Appl. Phys.* **2010**, *49*, 08JG02.
5. Chen, C. H. *Chem. Mater.* **2004**, *16*, 4389.
6. Lee, K. H.; Kim, Y. K.; Yoon, S. S. *Bull. Korean. Chem. Soc.* **2011**, *32*, 1391.
7. Lee, K. H.; Kim, Y. K.; Yoon, S. S. *Bull. Korean. Chem. Soc.* **2011**, *32*, 2787.
8. Zhang, X. H.; Chen, B. J.; Lin, X. Q.; Wong, O. Y.; Lee, C. S.; Kwong, H. L.; Lee, S. T.; Wu, S. K. *Chem. Mater.* **2001**, *13*, 1565.
9. Declercq, D.; Delbeke, P.; De Schryver, F. C.; Van Meervelt, L.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 5702.
10. Chen, C. H.; Tang, C. W.; Shi, J., Klubek, K. P. *Thin Solid Films* **2000**, *363*, 327.
11. Kang, H.-Y.; Lee, C. *J. Korean Phys. Soc*. **2004**, *45*, 756.
12. Kang, H.-Y.; Kang, G.-W.; Park, K.-M.; Yoo, I.-S.; Lee, C. *Mat. Sci. Eng. C- Mater.* **2004**, *24*, 229.
13. Hamada, Y.; Kanno, H.; Tsujioka, T.; Takahashi, H. *Appl. Phys. Lett.* **1999**, *75*, 1682.
14. Kim, B.-O.; Kim, C.-S.; Han, H.; Kim, S.-M.; Kim, J.-Y.; Cho, K.-S.; Jung, S.-Y.; Yun, S. S.; Kwon, H.-J.; Cho, Y.-J.; Kim, Y. K.; Kim, S.-M. *WO 121274*, 2005.