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Red Fluorescent Donor-π-Acceptor Type Materials based on Chromene Moiety for Organic Light-Emitting Diodes

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Two red emitters, 2-(7-(4-(diphenylamino)styryl)-2-methyl-4*H*-chromen-4-ylidene)malonitrile (**Red 1**) and 2-(7-(julolidylvinyl)-2-methyl-4*H*-chromen-4-ylidene)malonitrile (**Red 2**) have been designed and synthesized for application as red-light emitters in organic light emitting diodes (OLEDs). In these red emitters, the julolidine and triphenyl moieties were introduced to the emitting core as electron donors, and the chrome-derived electron accepting groups such as 2-methyl-(4*H*-chromen-4-ylidene)malononitrile were connected to electron donating moieties by vinyl groups. To explore the electroluminescence properties of these materials, multilayered OLEDs using red materials (**Red 1** and **Red 2**) as dopants in Alq$_3$ host were fabricated. In particular, a device using **Red 1** as the dopant material showed maximum luminous efficiencies and power efficiencies of 0.82 cd/A and 0.33 lm/W at 20 mA/cm^2. Also, a device using **Red 2** as a dopant material presented the CIEx,y coordinates of (0.67, 0.32) at 7.0 V.

Key Words : Red fluorescence, Donor-π-Acceptor, Chromene derivatives, OLED

Introduction

Push-pull red emitters with electron donor-π-electron acceptor type structures have been widely studied for the applications to organic light-emitting diodes (OLEDs).[1] Particularly, a variety of red fluorescent 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM) derivatives have been synthesized and their electroluminescent properties have been investigated.[2] However, these materials remain far below the requirements for full-color organic light-emitting diodes (OLEDs) in terms of EL efficiencies due to concentration quenching by excimer and exciplex formation.[3] Also, color purities of OLEDs using these materials need to be improved, because the significant portion of their emission spectra is in fact below 600 nm, and thus they cannot emit a saturated red color.[4]

Recently, our group has reported many red fluorescent materials based on 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) and 2-(2-(4-(diphenylamino)styryl)-4*H*-chromen-4-ylidene)-malononitrile (DCCPA), which have improved EL performances in comparison with DCM.[5-10] These materials have the bulky substituents to prevent concentration quenching and thus lead to the improved EL efficiencies of OLEDs using these materials. Furthermore, to improve the color purities, new materials with the extended π-conjugation lengths had been developed. However, their EL performance still requires improvement.

In this paper, we describe the synthesis and electroluminescent properties of red fluorescent donor-π-acceptor type materials based on chromene moiety such as **Red 1** and **2**.[11] In these red emitters, the julolidine and triphenyl moieties were introduced to the emitting core as electron donors, and

the chrome-derived electron accepting group such as 2-methyl-(4*H*-chromen-4-ylidene)malononitrile were connected to electron donating moieties by vinyl groups. As described below, the OLED devices using **Red 1** and **2** showed the efficienct electroluminescent properties.

Experimental Section

Synthesis and Charcterization ^{1}H- and ^{13}C-NMR were recorded on a Varian (300 or Unity Inova 300Nb or Unity Inova 500Nb) spectrometer. Low- and high-resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in the FAB mode and a Jeol JMS-600W spectrometer in the EI mode and a JMS-T100TD (AccuTOF-TLC) in the positive ion mode. 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 LUMO energy levels were estimated by subtracting the energy gap from the HOMO energy levels.

Synthesis of Red 1 [(2-(7-(4-(diphenylamino)styryl)-2-methyl-4*H*-chromen-4-ylidene)malonitrile)]. To a solution of 3 mL of tributylamine were added 0.3 g of compound **1** (1.10 mmol), 0.264 g of compound **2** (1.10 mmol),[13] 0.014 g of Pd(OAc)$_2$ (0.0660 mmol) and 0.133 g of P(*o*-tol)$_3$ (0.440 mmol). The reaction mixture was refluxed under nitrogen atmosphere for 18 h. The mixture was washed with brine and extracted with dichloromethane. After the evaporation of solvent, the resulting products were purified by silica-gel column chromatography with the elution of ethyl

acetate and hexane (1:15) to afford 0.409 g of the chromene intermediate (0.955 mmol, 86.8% yield). To a solution of 0.4 g of the chromene intermediate (0.931 mmol) in acetic anhydride (10 mL) was added 0.085 g of malonitrile (1.30 mmol) and then refluxed for 15 h. The solution was washed with brine and extracted with CH_2Cl_2. After solvent evaporation, silica-gel column chromatography with the elution of ethyl acetate and hexane (1:2) provided 0.183 g (0.358 mmol, 38.5%) of **Red 1** as yellowish solids. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 2.11 (s, 3H), 5.30 (s, 1H), 6.80 (d, 1H, J = 16.5 Hz), 6.98 (d, 2H, J = 8.0 Hz), 7.01 (s, 1H), 7.07 (d, 2H, J = 8.50 Hz), 7.37 (s, 1H), 7.48 (t, 2H, J = 9.0 Hz), 7.50 (d, 1H, J = 8.0 Hz), 7.51 (d, 4H, J = 8.0 Hz), 7.78 (d, 2H, J = 8.50 Hz), 8.78 (d, 1H, J = 8.50 Hz); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 142.2, 138.1, 136.8, 135.1, 133.9, 132.1, 130.8, 129.6, 128.1, 126.7, 125.3, 124.2, 122.3, 121.5, 120.2, 118.9, 117.1, 116.3, 115.1, 114.2, 112.9, 31.3; Mass (EI) m/z = 477 (M$^+$); HRMS (EI) calcd for C$_{33}$H$_{23}$N$_3$O, 477.1841; found, 477.1837.

Synthesis of Red 2 [(2-(7-(julolidylvinyl)-2-methyl-4*H*-chromen-4-ylidene)malonitrile)]. To a solution of 0.3 g of compound **3** (1.25 mmol), 71 mg of Pd(PPh$_3$)$_4$ (0.062 mmol) and 0.16 g of LiCl (3.75 mmol) in 10 mL of toluene was added 0.51 g of tributylvinyltin (1.375 mmol). The reaction mixture was refluxed under nitrogen atmosphere for 16 h. The mixture was washed with aqueous KF solution and extracted with dichloromethane. After the evaporation of solvent, the resulting products were purified by silica-gel column chromatography with the elution of ethyl acetate and hexane (1:2) to afford 0.19 g of compound **4** (1.03 mmol, 82.0% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 2.38 (s, 3H), 5.44 (d, 1H, J = 8.0 Hz), 5.89 (d, 1H, J = 8.0 Hz), 6.16 (s, 1H), 6.73 (m, 1H), 6.83 (s, 1H), 7.39 (d, 1H, J = 8.0 Hz), 8.10 (d, 1H, J = 8.0 Hz); Mass (EI) m/z = 186 (M$^+$).

To a solution of 3 mL of tributylamine were added 016 g of compound **4** (0.86 mmol), 0.216 g of 4-bromojulolidine (0.86 mmol), 0.011 g of Pd(OAc)$_2$ (0.0510 mmol) and 0.103 g of P(o-tol)$_3$ (0.340 mmol). The reaction mixture was refluxed under nitrogen atmosphere for 18 h. The mixture was washed with brine and extracted with dichloromethane. After the evaporation of solvent, the resulting products were purified by silica-gel column chromatography with the elution of ethyl acetate and hexane (1:15) to afford 0.23 g of chromene intermediate (0.642 mmol, 74.7% yield). To a solution of 0.2 g of the chromene intermediate (0.56 mmol) in acetic anhydride (10 mL) was added 0.052 g of malonitrile (0.784 mmol) and then refluxed for 15 h. The solution was washed with brine and extracted with CH_2Cl_2. After solvent evaporation, silica-gel column chromatography with the elution of ethyl acetate and hexane (1:2) provided 0.110 g (0.270 mmol, 48.2%) of **Red 2** as redish solids. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 1.97 (m, 4H), 2.11 (s, 3H), 2.77 (t, 4H, J = 6.2 Hz), 3.22 (t, 4H, J = 6.0 Hz), 5.30 (s, 1H), 6.80 (d, 1H, J = 16.5 Hz), 7.01 (s, 1H), 7.10 (d, 1H, J = 16.50 Hz), 7.37 (s, 1H), 7.50 (d, 1H, J = 8.0 Hz), 8.78 (d, 1H, J = 8.50 Hz); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 141.5, 137.5, 134.5, 132.3, 131.2, 129.7, 127.3, 125.8, 123.1, 121.8, 120.5, 119.2, 118.3,

117.6, 115.6, 114.5, 113.8, 42.1, 32.5, 31.2, 29.7; Mass (EI) m/z = 405 (M$^+$); HRMS (EI) calcd for C$_{27}$H$_{23}$N$_3$O, 405.1841; found, 405.1832.

Fabrication of OLED. 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$_2$ gas. The device structures were as follows: ITO/*N,N'*-diphenyl-*N,N'*-(1-napthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) (50 nm)/tris(8-quionlinolato)-aluminium (Alq$_3$) : Red dopants (2 or 5%) (30 nm)/bathucuproine (BCP) (10 nm)/Alq$_3$ (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 1'Éclairage (CIE) coordinate characteristics were measured using a Keithly 2400 source measurement unit and a Chroma meter MINOLTA CS-1000A. Electro-luminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

The synthetic routes for red emitters **Red 1** and **2** are shown in Scheme 1. These red emitters were obtained by Heck reaction between the vinyl intermediates[13] and the corresponding bromo intermediates, and then subsequent Knoevenagel condensation with malonitrile.[14] These compounds were fully characterized by ^{1}H- and ^{13}C-NMR, FT-IR, and low- and high-resolution mass spectroscopy.

The ultraviolet-visible (UV-Vis) absorption spectra of **Red 1**, **Red 2** and comparative material **DCCPA** are shown in Figure 1(a). The maximum absorption peaks of these red materials were 453, 495 and 502 nm, respectively. Figure
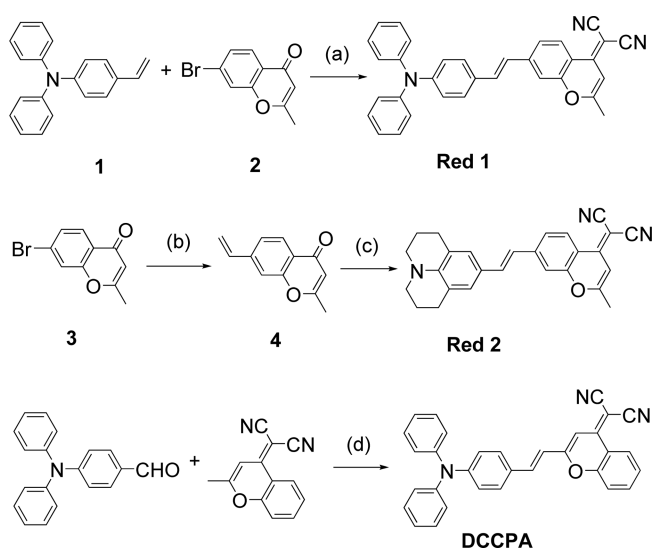
Scheme 1. Synthesis and structures of the red materials **Red 1, 2** and **DCCPA**. (a) i) Pd(OAc)$_2$, P(o-tol)$_3$, Tributylamine. ii) Malonitrile, Ac$_2$O. (b) Tributylvinyltin, Pd(PPh$_3$)$_4$. (c) 4-bromojulolidine, Pd(OAc)$_2$, P(o-tol)$_3$, Tributylamine. ii) Malonitrile, Ac$_2$O. (d) Piperidine/EtOH, reflux.
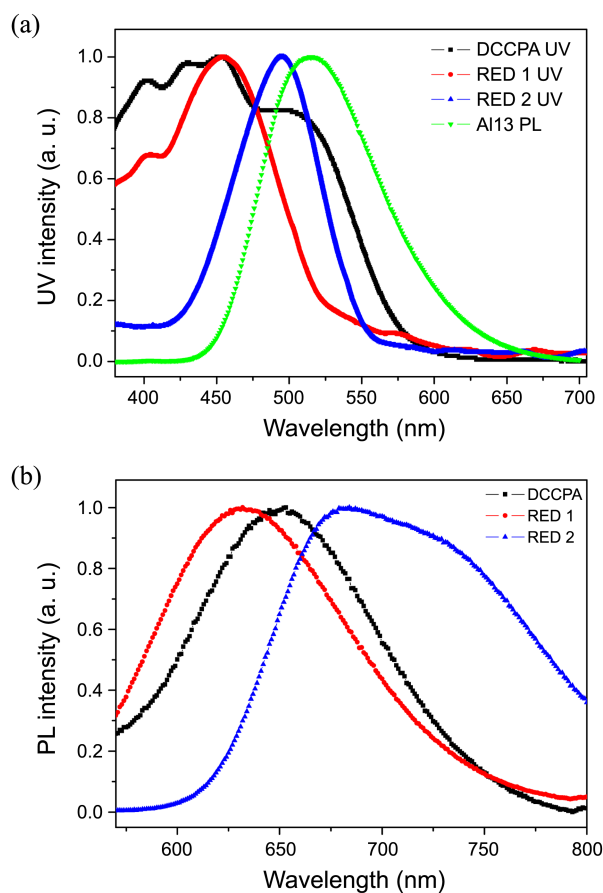
(a)

(b)

Figure 1. (a) UV-Vis and (b) PL spectra of red emitters **Red 1**, **2** and **DCCPA**.

1(a) shows the good overlap between the emission spectra of a common fluorescent red host material Alq_3 and the absorption spectra of **Red 1** and **2**. This observation indicated that the Förster singlet energy transfer from host Alq_3 to red emitters **Red 1** and **2** would be efficient, and thus Alq_3 is a suitable host in the OLEDs by using these compounds as red

dopant materials. **Red 1** and **2** exhibit efficient red emissions with maximum emission peaks of 632 and 684 nm, respectively, as shown in Figure 1(b). The PL quantum yields of **Red 1** and **2** were 0.73 and 0.25, respectively. **Red 2** showed the deeper red emission peak than **Red 1**. Presumably, the stronger electron donating properties of julolidine than triphenyl moiety would lead the red-shifted emission of **Red 2** in comparison with **Red 1**. The HOMO/LUMO levels for **Red 1** and **2** were -5.55/-3.37 and -5.45/-3.50, respectively. All physical properties were summarized in Table 1.

To explore the electroluminescence properties of these materials, multilayered OLED devices **1-4** were fabricated, device Structure; ITO/*N,N'*-diphenyl-*N,N'*-(1-napthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) (50 nm)/tris(8-quionlinolato)-aluminium (Alq_3) : Red dopants (30 nm)/bathucuproine (BCP) (10 nm)/Alq_3 (40 nm)/Liq (2 nm) / Al. In devices **1-4**, **Red 1-2** and **DCCPA** were used as dopants in the Alq3 host. NPB, Alq3 and Liq were used as hole-transporting layer, electron-transporting layer and electron-injection layer, respectively. Also, BCP was used as a hole blocking layer to prevent hole leakage to the electron-transporting layer and thus improve the EL efficiencies.

Figure 2 presents the (a) Current density-voltage and (b) luminance-voltage characteristics of devices **1-4**. The Maximum brightness of these red devices exhibited 1180, 304, 114 and 792 cd/m^2 respectively, at 10.5 V. The luminous efficiencies, power efficiencies of devices **1-4** are shown in Figure 3 and also all electroluminescence data are summarized in Table 2. The luminous efficiencies of devices **1-4** were 0.82, 0.50, 0.18 and 0.77 cd/A, respectively, at 20 mA/cm^2. And power efficiencies of devices **1-4** were 0.33, 0.24, 0.07 and 0.21 lm/W, respectively, at 20 mA/cm^2. Notably, compared to device **4** using **DCCPA** as dopant, the luminous and power efficiency of device **1** using **Red 1** increased by 6% and 57% at 20 mA/cm^2, respectively.

However, the luminous and power efficiency of device **3** using **Red 2** decreased by 77% and 67% at 20 mA/cm^2,

Table 1. Photophysical properties of **Red 1**, **2** and **DCCPA**

Compound	UV_{Max} (nm)[a]	PL_{Max} (nm)[a]	FWHM	HOMO (eV)[b]	LUMO (eV)[b]	E_g	Q.Y[c]
Red 1	453	632	108	-5.55	-3.37	2.18	0.63
Red 2	495	684	139	-5.45	-3.50	1.95	0.15
DCCPA	502	650	105	-5.60	-3.45	2.15	0.54

[a,b]Maximum absorption or emission wavelength in 1,2-dichloroethane (*ca.* 1×10^{-5} M). [b]Obtained from AC-2 and UV-vis absorption measurements. [c]Using DCJTB as a standard; λ_{ex} = 500 nm (Φ = 0.78 in 1,2-dichloroethene).

Table 2. EL performance characteristic of devices **1-4**

Devices	Dopant (doping %)	L^a (cd/m^2)	LE-J[b/c] (cd/A)	PE[b/c] (lm/W)	EL[d] (nm)	CIE[d] (x,y)
1	**Red 1 (2)**	1180	0.82/1.25	0.33/0.80	603	(0.59, 0.40)
2	**Red 1 (5)**	304	0.50/0.58	0.24/0.55	616	(0.61, 0.38)
3	**Red 2 (2)**	114	0.18/0.84	0.07/0.44	679	(0.67, 0.32)
4	**DCCPA (2)**	792	0.77/0.81	0.21/0.30	624	(0.64, 0.36)

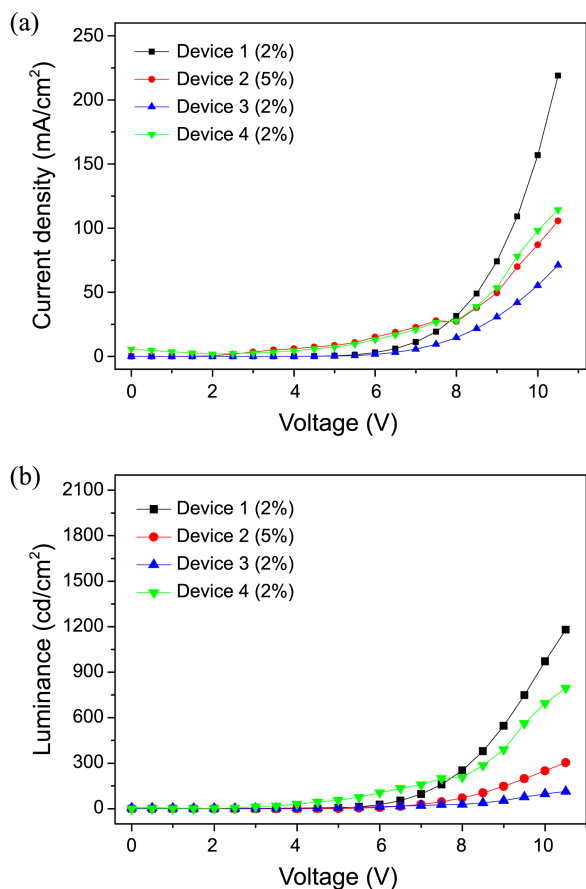[a]Maximum luminance at 10.5 V. [b]Value measured at 20 mA/cm^2. [c]Maximum values. [d]Value measured at 7.0 V.

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

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

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

respectively, in comparison with device **4**. The EL efficiencies are increased by the order of devices **1** > **4** > **3**, which is compatible with the order of quantum efficiencies of dopants **Red 1**, **DCCPA** and **Red 2** in the corresponding devices, as shown in Table 1. These observations imply that the quantum efficiencies of the emitting materials play an important role in the EL efficiencies of devices.

In devices **1** and **2**, using **Red 1** as a dopant at different doping concentrations, the increase in doping concentration reduced EL efficiencies. For example, device **1** with 2% doping concentration of **Red 1** showed the luminous efficiency of 0.82 cd/A and the power efficiency 0.33 lm/W at 20 mA/cm^2, respectively. On the other hand, device **2** with 5% doping concentration of **Red 1** exhibited the luminous efficiency of 0.50 cd/A and the power efficiency 0.24 lm/W at 20 mA/cm^2, respectively. The luminous and power efficiencies of device **2** were decreased by 39% and 27% at 20 mA/cm^2, respectively, in comparison to those of device **1**.

Presumably, concentration quenching at the high doping concentration of **Red 1** lead to reduced device EL efficiencies. Interestingly, this hypothesis was verified through the EL spectra of devices **1** and **2**. EL spectrum of device **2** with the high doping concentration of **Red 1** showed the redshift by 13 nm in comparison with that of device **1**. This observation implies that Red 1 formed excimers at high doping concentration, which lead the reduced EL effici-
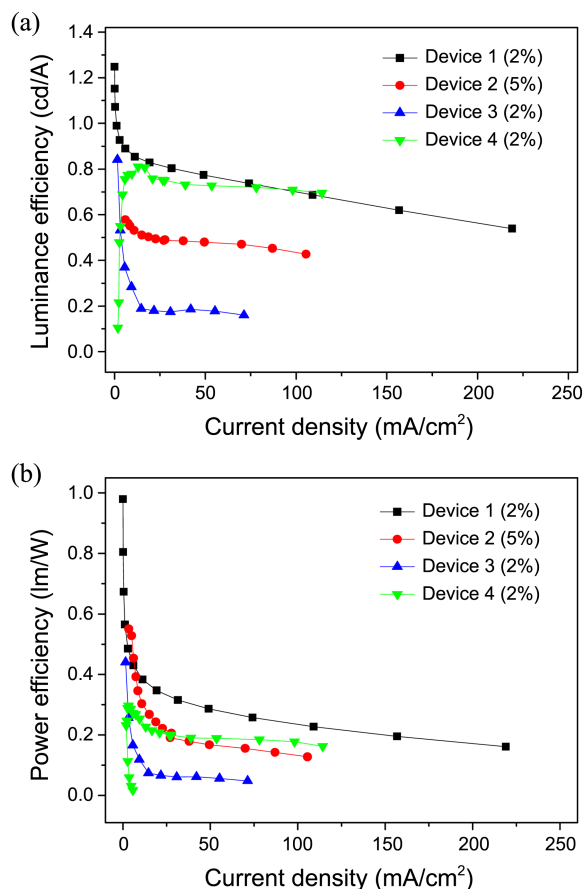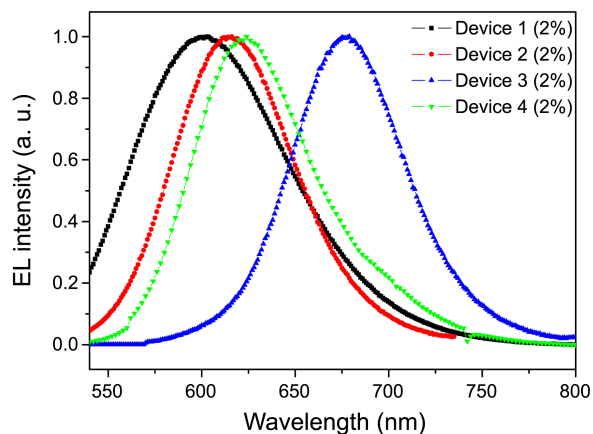
encies.

The electroluminescent emission spectra of devices **1-4** are shown in Figure 4. The EL spectrum of device exhibited red emissions with the maximum emission peaks of 603, 615, 679 and 624 nm, rspectively. This trend is in good agreement with the result of the PL spectra of **Red 1**, **2** and **DCCPA**. In particular, compared to device **4** using **DCCPA**, device **3** using **Red 2** showed the deeper red emission with a Commission Internationale de l'Eclairage (CIE$_y$) coordinates of (0.67, 0.32), it was close to the standard red CIE coordi-

nates (0.67, 0.33) of the national television systems committee (NTSC). Thus, this study clearly demonstrated the excellent properties of donor-π-acceptor type red materials based on chromene moiety for application in red-emitting materials in OLEDs.

Conclusions

We have synthesized two novel red dopants for applications in organic light emitting diode (OLEDs), by introducing a triphenylamine and julolidine segment as an electron donor, and chromene moiety as a electron acceptor in donor-π-acceptor type emitting core. It has demonstrated that a device using **Red 1** as a dopant showed a bright red emission with maximum luminance of 0.82 cd/A and power efficiency of 0.33 lm/W at 20 mA/cm^2, which are much higher than a device using **DCCPA**. In particular, a device using **Red 2** as a dopant showed deep red emission with the CIE coordinates of (x = 0.67, y = 0.32) at 7.0 V, which is close to the standard red CIE coordinates of national television systems committee (x = 0.67, y = 0.33).

References and Notes

1. *Organic Light-Emitting Materials and Devices*; Li, Z.; Meng, H. Eds.; Taylor & Francis: Boca Raton, USA. 2007; p 295.
2. Chen, C. H. *Chem. Mater.* **2004**, *16*, 4389.
3. Chen, C. H.; Tang, C. W.; Shi, J.; Klubek, K. P. *Thin Solid Films* **2000**, *363*, 327.
4. Zhao, P.; Tang, H.; Zhang, Q.; Pi, Y.; Xu, M.; Sun, R.; Zhu, W. *Dyes and Pigments* **2009**, *82*, 316.
5. Lee, K. H.; Kim, S. M.; Kim, J. Y.; Kim, Y. K.; Yoon, S. S. *Bull. Korean. Chem. Soc.* **2010**, *31*, 2884.
6. 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.
7. Lee, K. H.; Park, M. H.; Kim, S. M.; Kim, Y. K.; Yoon, S. S. *Jpn. J. Appl. Phys.* **2010**, *49*, 08JG02.
8. Lee, K. H.; Kim, Y. K.; Yoon, S. S. *Bull. Korean Chem. Soc.* **2011**, *32*, 1391.
9. Lee, K. H.; Kim, C. S.; Kim, Y. K.; Yoon, S. S. *Thin Solid Films* **2012**, *520*, 3946.
10. Lee, K. H.; Kim, Y. K.; Yoon, S. S. *Bull. Korean Chem. Soc.* **2011**, *32*, 4419.
11. Yao, Y.-S.; Zhou, Q.-X.; Wang, X.-S.; Wang, Y.; Zhang, B.-W. *Adv. Func. Mater.* **2007**, *17*, 93.
12. Chen, C. H.; Tang, C. W.; Shi, J., Klubek, K. P. *Macromol. Symp.* **1998**, *125*, 49.
13. Rao, A. V. S.; Rao, N. V. S. *Indian Acad. Sci. Section A* **1970**, *72*, 24.
14. 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.