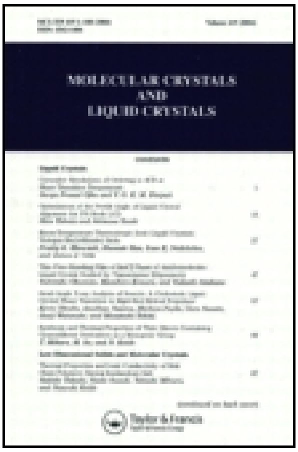


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Electroluminescent Properties of t-Butylated 2-(2-(4-(Diarylamino)styryl)-4H-chromen-4-ylidene)malononitrile Derivatives for OLED

Kum Hee Lee [a], Jin Soo Hwang [a], Min Hye Park [a], Hyuck Joo Kwon [b], Young Kwan Kim [b] & Seung Soo Yoon [a]

[a] Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea

[b] Department of Information Display, Hongik University, Seoul, 121-791, Korea

Version of record first published: 18 Oct 2011

To cite this article: Kum Hee Lee, Jin Soo Hwang, Min Hye Park, Hyuck Joo Kwon, Young Kwan Kim & Seung Soo Yoon (2011): Synthesis and Electroluminescent Properties of t-Butylated 2-(2-(4-(Diarylamino)styryl)-4H-chromen-4-ylidene)malononitrile Derivatives for OLED, Molecular Crystals and Liquid Crystals, 550:1, 250-259

To link to this article: http://dx.doi.org/10.1080/15421406.2011.599771

Mol. Cryst. Liq. Cryst., Vol. 550: pp. 250–259, 2011
Copyright © Sungkyunkwan University
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.599771

Synthesis and Electroluminescent Properties of *t*-Butylated 2-(2-(4-(Diarylamino)styryl)-4*H*-chromen-4-ylidene)malononitrile Derivatives for OLED

KUM HEE LEE,[1] JIN SOO HWANG,[1] MIN HYE PARK,[1]
HYUCK JOO KWON,[2] YOUNG KWAN KIM,[2,*]
AND SEUNG SOO YOON[1,*]

[1]Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea
[2]Department of Information Display, Hongik University, Seoul 121-791, Korea

*We designed and synthesized new red fluorescent materials based on t-butylated 2-(2-(4-(diarylamino)styryl)-4H-chromen-4-ylidene)malononitrile derivatives (**3a**-**3d**). A device using 2-(6,8-di-tert-butyl-2-(4-((4-tert-butylphenyl)(2,7-di-tert-butyl-9,9-diethyl-9H-fluoren-4-yl)amino)styryl)-4H-chromen-4-ylidene)malononitrile (**3a**) as a dopant showed efficient red electroluminescent properties with a maximum luminance of 3357 cd/m^2 at 15.0 V, and maximum luminous and power efficiencies of 1.12 cd/A and 0.60 lm/W, respectively. The CIE coordinates of this device using this material was (0.64, 0.35) at 7.0 V, and this device also showed stable color chromaticity at various voltages.*

Keywords OLED; Red fluorescence; chromene groups; *tert*-Butyl groups.

Introduction

During the past decades, significant advances have been made in organic light-emitting diodes (OLEDs) for applications in flat panel displays and solid-state lighting [1]. Although many research efforts have been focused on the development of the emitting materials [2–6], red fluorescent emitting materials remain far below the requirements for full-color organic light-emitting diodes (OLEDs) in terms of both color purity and efficiency [7]. For example, a variety of red fluorescent materials including pyran containing materials, such as DCM (4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran) and DCJTB (4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran), have been studied widely [8, 9]. However, their EL performance, such as EL efficiency and CIE coordinates, are not pleased with a prerequisite for practical applications.

Recently, Lee et al. reported an OLED device with red electroluminescence, a power efficiency of 0.139 lm/W and CIE coordinates of (0.60, 0.39) using a new red fluorescent material, 2-(2-(4-(diphenylamino)styryl)-4H-chromen-4-ylidene)malononitrile (DCCPA),

---

[*] Corresponding author. E-mail: ssyoon@skku.edu (Seung Soo Yoon), kimyk@hongik.ac.kr (Young Kwan Kim)

as a dopant [10]. Furthermore, 2-(2-(4-(diphenylamino)styryl)-4H-6,7-dimethyl-chromen-4-ylidene)malononitrile (DCCMPA) showed improved EL performance due to the introduction of two methyl substituents on the chromene moiety by preventing concentration quenching [11]. However, their EL performance still requires improvement.

In this paper describes the synthesis and electroluminescent properties of red fluorescent materials **3a-3d**. In red emitters **3a-3d**, the bulky t-butyl groups were introduced to the DCCPA skeleton to increase the steric hindrance between red emitters in the emitting layer of the devices and improve the EL performance by preventing concentration quenching.

Experimental

Materials and Measurement

^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra were recorded on a Varian (300 or Unity Inova 300Nb or Unity Inova 500Nb) 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 these 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 by low energy photo-electron spectroscopy (Riken-Keiki AC-2). The LUMO energy levels were estimated by subtracting the energy gap from the HOMO energy levels.

(6,8-di-tert-butyl-2-methyl-4H-chromen-4-ylidene)malononitrile. (**1**) Acetyl chloride (2.01 mmol) was added to a solution of NaH (5.03 mmol) and 1-(3,5-di-tert-butyl-2-hydroxy phenyl)ethanone (2.01 mmol) in anhydrous THF at room temperature. The mixture was stirred for 1 h and NH_4Cl was added at 0°C. The solution was extracted with hexane and brine. Without further purification, the resulting materials were dissolved in glacial acetic acid (5 ml) and HCl (1 ml) and heated to 100°C for 1 h. After cooling to room temperature, the reaction mixture was washed with $NaHCO_3$ and extracted with ethyl acetate and brine. After filtration and solvent evaporation, the mixture was purified by silica gel column chromatography with ethyl acetate and hexane (1:4). (Yield : 87%) The resulting compound (0.73 mmol) and malonitrile (1.50 mmol) were dissolved in acetic anhydride and heated to 24 h. The solution was washed with $NaHCO_3$ and extracted with CH_2Cl_2. After filtration and solvent evaporation, the mixture was purified by re-crystallization with CH_2Cl_2 and hexane. The obtained compound was a yellowish solid (Yield : 79%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 8.79 (d, J = 2.2 Hz, 1H), 7.75 (d, J = 2.2 Hz, 1H), 6.75 (d, J = 0.4 Hz, 1H), 2.49 (s, 3H), 1.49 (s, 9H), 1.38 (s, 9H); ^{13}C-NMR (125 MHz): δ ppm 160.5, 155.0, 150.0, 148.7, 138.9, 126.0, 122.8, 120.5, 120.3, 105.5, 61.5, 35.8, 35.7, 31.6, 31.6, 31.5, 30.4, 30.3; FT-IR (KBr): $\nu = 2970, 2360, 2342, 1643, 1608, 1572, 1485, 1462, 1396, 1371, 1361, 836$ cm^{-1}; Mass (EI) m/z = 320 (M^+).

4-((4-tert-butylphenyl)(2,7-di-tert-butyl-9,9-diethyl-9H-fluoren-4-yl)amino)benzalde-hyde. (**2a**) 2-(4-Bromophenyl)-1,3-dioxolane (2.66 mmol) and 4-bromo-2,7-ditertbuthyl fluorene (1.33 mmol) were dissolved to anhydrous toluene (5 ml). Pd_2dba_3 (0.007 mmol), 2-(di-tert-butylphosphino)-biphenyl (0.13 mmol) and Na-O-(t-Bu) (3.99 mmol) were then added to this solution under an Ar atmosphere. The reaction mixture was heated to 80°C for 5 hr. 4-tert-butylaniline (1.33 mmol) was then added and heated to 80°C overnight. After the reaction had finished, the reaction mixture was extracted with diethyl ether and brine. The organic layer was dried with $MgSO_4$ and filtered. The solvent was then evaporated. The mixture was purified by silica column chromatography with ethyl acetate and hexane. The product was obtained as a reddish solid (Yield: 55%). ^{1}H-NMR (300 MHz, $CDCl_3$); δ ppm 1.05 (m, 6H), 1.25 (s, 9H), 1.30 (s, 9H), 1.34 (s, 9H), 2.02 (m, 4H), 6.84 (d, $J = 9.0$ Hz, 2H), 7.06 (d, $J = 9.0$ Hz, 2H), 7.33 (m, 5H), 7.50 (d, $J = 9.0$ Hz, 2H), 7.61 (m, 2H), 9.72 (s, 1H); ^{13}C-NMR (125 MHz): δ ppm 190.4, 157.3, 142.4, 140.1, 138.7, 136,3, 135.7, 134.2, 131.6, 129.8, 129.3, 127.2, 126.5, 125.3, 122.3, 121.4, 121.1, 120.2, 119.2, 118.3, 116.2, 56.9, 38.7, 38.5, 35.7, 35.3, 32.3, 31.8, 31.2, 30.9, 8.7, 8.4; Mass (FAB) *m/z* = 585 (M^+).

4-((3,5-di-tert-butylphenyl)(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)amino)benzaldehyde. **(2b)** Compound **2b** was prepared by method of compound **2a** using 2-bromo-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene and 3,5-di-tert-butylaniline. The obtained compound was yellow solid (Yield : 48%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 1.24 (s, 18H), 1.36 (s, 12H) 1.57 (m, 4H), 6.95 (m, 4H), 7.24 (m, 3H), 7.70 (m, 3H), 9.80 (s, 1H); ^{13}C-NMR (125 MHz): δ ppm 191.1, 159.3, 147.8, 145.4, 143.2, 134.7, 132.1, 130.5, 128.7, 126.8, 125.2, 124.3, 123.3, 122.1, 120.9, 36.2, 35.7, 34.9, 34.5, 34.3, 32.2, 31.9, 30.7; Mass (FAB) *m/z* = 495 (M^+).

4-(Bis(3,5-di-tert-butylphenyl)amino)benzaldehyde. **(2c)** Compound **2c** was prepared by method of compound **2a** using 1-bromo-3,5-di-tert-butylbenzene and 3,5-di-tert-butylaniline. The obtained compound was yellow solid (Yield : 39%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 1.15 (s, 18H), 1.24 (s, 18H), 7.01 (m, 4H), 7.03 (m, 2H), 7.67 (m, 2H), 9.80(s, 1H). ^{13}C-NMR (125 MHz): δ ppm 190.7, 159.3, 147.3, 145.2, 139.3, 137.7, 129.3, 127.6, 122.5, 34.7, 30.1; Mass (FAB) *m/z* = 497 (M^+).

4-((4-tert-butylphenyl)(3,7-di-tert-butylnaphlen-2-yl)amino)benzaldehyde. **(2d)** Compound **2d** was prepared by method of compound **2a** using 1-bromo-3,7-di-tert-buthylnaphthalene and 4-tert-butylaniline. The obtained compound was yellowish solid (Yield : 60%). ^{1}H-NMR (300 MHz, $CDCl_3$); δ ppm 1.22 (s, 9H), 1.27 (s, 9H) 1.33 (s, 9H), 6.91 (d, $J = 9.0$ Hz, 2H), 7.18 (d, $J = 9.0$ Hz, 2H), 7.30 (d, $J = 9.0$ Hz, 2H), 7.49(s, 1H), 7.63 (d, $J = 9.0$ Hz, 2H), 7.71 (s, 2H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 8.5$ Hz, 1H), 9.77 (s, 1H); ^{13}C-NMR (125 MHz): δ ppm 189.7, 155.1, 147.5, 133.2, 132.6, 131.5, 130.3, 129.3, 126.3, 125.1, 124.1, 122.7, 121.5, 120.3, 119.2, 118.0, 116.4, 115.2, 110.2, 35.9, 35.1, 34.6, 31.9, 31.6, 31.0; Mass (FAB) *m/z* = 491 (M^+).

2-(6,8-di-tert-butyl-2-(4-((4-tert-butylphenyl)(2,7-di-tert-butyl-9,9-diethyl-9H-fluoren-4-yl)amino)styryl)-4H-chromen-4-ylidene)malononitrile. **(3a)** To a solution of compound **1** (0.26 mmol) and **2a** (0.26 mmol) in anhydrous ethyl alcohol (10 ml) was added piperidine (1.17 mmol) and then heated to 140°C for 5 h with dean-stark trap. After cooling in refrigerator, the mixture was filtered with hexane and extracted with ethyl acetate and brine. After evaporation of 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: 43%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 8.81 (d, $J = 1.5$ Hz, 1H), 7.75 (s, 1H), 7.63 (m, 1H), 7.50 (m, 8H), 7.22 (m, 2H), 7.12 (m, 2H), 6.93 (m, 3H), 6.63 (d, $J = 15.8$ Hz, 1H), 2.05 (d, $J = 7.0$ Hz, 5H), 1.39 (s, 12H), 1.32 (t, $J = 4.2$ Hz, 31H), 0.39 (s, 7H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ ppm 158.2, 154.6, 152.8, 152.4, 150.3, 150.1, 149.5, 148.3, 147.1, 143.1, 139.2, 138.5, 138.3, 137.1, 137.0, 131.8, 130.1, 130.0, 129.8, 128.4, 126.7, 126.5, 125.6, 124.8, 124.2, 123.8, 122.1, 120.5, 119.5, 117.7, 116.0, 115.1, 65.6, 56.3, 35.8, 35.7, 35.2, 35.0, 34.6, 31.8, 31.6 8.9; FT-IR (KBr): $\nu = 2969, 2342, 1508, 1496, 1457, 1177, 832$ cm^{-1}; Mass (EI) *m/z* = 887 (M^+); HRMS (EI) calcd for $C_{63}H_{73}N_3O$, 887.5754; found, 887.5761; mp: 176°C.

2-(6,8-di-tert-butyl-2-(4-((3,5-di-tert-butylphenyl)(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)amino)styryl)-4H-chromen-4-ylidene)malononitrile. **(3b)** Compound **3b** was prepared by method of **3a** using **2b** instead of **2a**. The obtained compound was reddish solid (Yield : 52%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 8.81 (d, $J = 2.1$ Hz, 1H), 7.76 (d, $J = 2.1$ Hz, 1H), 7.65 (d, $J = 15.8$ Hz, 1H), 7.40 (d, $J = 8.8$ Hz, 2H), 7,24 (d, $J = 8.8$ Hz, 1H), 7.20 (m, 2H), 7.08 (m, 6H), 6.90 (m, 2H), 6.76 (m, 1H), 1.69 (s, 3H), 1.59 (s, 8H), 1.47 (s, 2H), 1.40 (s, 9H), 1.28 (d, $J = 6.5$ Hz, 21H), 1.19 (s, 5H). ^{13}C-NMR (125 MHz): δ ppm 158.1, 154.6, 152.2, 151.0, 149.5, 148.4, 146.2, 146.0, 143.9, 141.1, 138.9, 138.6, 130.2, 129.3, 127.6, 126.6, 123.4, 122.8, 120.8, 120.5, 118.6, 118.1, 118.0, 117.0, 115.8, 106.2, 35.8, 35.8, 35.3, 35.2, 34.6, 34.2, 32.1, 31.6, 31.5, 30.5, 30.3; FT-IR (KBr): $\nu = 2969$, 2342, 1588, 1561, 1507, 1496, 1316, 832 cm^{-1}; Mass (EI) $m/z = 797$ (M^+); HRMS (EI) calcd for $C_{56}H_{67}N_3O$, 797.5284; found, 797.5281; mp: 276.

2-(2-(4-(bis(3,5-di-tert-butylphenyl)amino)styryl)-6,8-di-tert-butyl-4H-chromen-4-ylidene)malononitrile. **(3c)** Compound **3c** was prepared by method of **3a** using **2c** instead of **2a**. The obtained compound was reddish solid (Yield : 56%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 8.81 (t, $J = 2.3$ Hz, 1H), 7.76 (d, $J = 1.6$ Hz, 2H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.16 (t, $J = 1.5$ Hz, 2H), 7.08 (d, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 1.8$ Hz, 3H), 6.88 (s, 1H), 6.76 (m, 1H), 1.56 (s, 10H), 1.49 (s, 5H), 1.39 (d, $J = 3.8$ Hz, 11H), 1.27 (s, 28H); ^{13}C-NMR (125 MHz): δ ppm 158.0, 154.6, 152.0, 150.9, 149.5, 148.4, 146.1, 138.9, 138.6, 130.2, 129.2, 126.8, 121.2, 120.5, 120.3, 120.2, 118.2, 118.1, 118.0, 117.0, 116.0, 106.3, 105.6, 35.8, 35.8, 35.2, 31.6, 31.5, 31.5, 30.5, 30.3; FT-IR (KBr): $\nu = 2209$, 1585, 1561, 1508, 1496, 1310, 838 cm^{-1}; Mass (EI) $m/z = 799$ (M^+); HRMS (EI) calcd for $C_{56}H_{69}N_3O$, 799.5441; found, 799.5436; mp: 280°C.

2-(6,8-di-tert-butyl-2-(4-((4-tert-butylphenyl)(3,7-di-tert-butylnaphthalen-1-yl)amino)styryl)-4H-chromen-4-ylidene)malononitrile. **(3d)** Compound **3d** was prepared by method of **3a** using **2d** instead of **2a**. The obtained compound was reddish solid (Yield : 70%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 8.80 (d, $J = 1.9$ Hz, 1H), 7.80 (d, $J = 8.7$ Hz, 1H), 7.73 (dd, $J = 2.2$, 9.8 Hz, 3H), 7.60 (d, $J = 15.8$ Hz, 1H), 7.53 (m, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.30 (s, 1H), 7.26 (d, $J = 3.8$ Hz, 2H), 7.14 (d, $J = 8.7$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 2H), 6.86 (s, 1H), 6.66 (d, $J = 15.8$ Hz, 1H), 1.40 (s, 13H), 1.37 (s, 12H), 1.30 (s, 10H), 1.18 (s, 10H); ^{13}C-NMR (125 MHz): δ ppm 158.0, 154.6, 151.5, 149.5, 148.9, 148.4, 146.9, 144.1, 142.1, 138.9, 138.5, 133.6, 130.2, 129.5, 128.8, 128.3, 126.3, 126.1, 125.2, 123.8, 122.0, 120.5, 119.4, 119.2, 118.1, 117.0, 115.7, 106.1, 35.8, 35.7, 35.1, 35.1, 34.6, 31.6, 31.5, 31.4, 31.3, 30.4; FT-IR (KBr): $\nu = 2969$, 2341, 1592, 1560, 1509, 1494, 1228, 677 cm^{-1}; Mass (EI) $m/z = 793$ (M^+); HRMS (EI) calcd for $C_{56}H_{63}N_3O$, 793.4971; found, 793.4977; mp: 177°C.

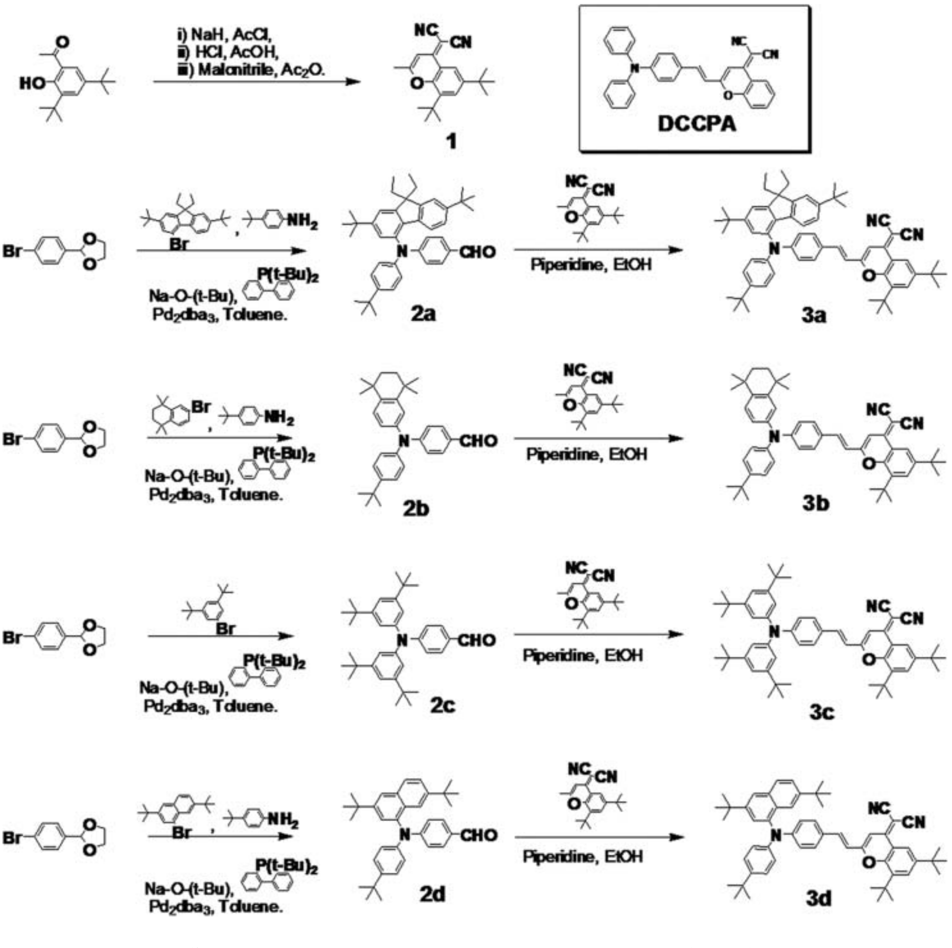
Device Fabrication and Characterization

OLEDs using the red-light-emitting molecules were fabricated by vacuum (10^{-6} torr) thermal evaporation onto pre-cleaned ITO coated glass substrates. The indium tin oxide (ITO) was first cleaned with acetone, methyl alcohol, distilled water and kept in isopropyl alcohol for 48 h and dried with N_2 gas. The structure was 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 material **3a** (2%) (30 nm)/bathucuproine (BCP) (10 nm)/Alq_3 (40 nm)/Liq (2 nm)/Al. All the device properties, such as the current density (J), luminance (L), luminance efficiency (LE), power efficiency (PE), and Commision Internationale De L'Eclairage ($CIE_{x,y}$) coordinates were measured using a Keithly 2400 source measurement unit and a

Chroma meter MINOLTA CS-1000A. The electro-luminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

Scheme 1 shows the structures and synthetic scheme of red emitters **3a**-**3d**. Synthesis of the red emitters **3a**-**3d** began with the preparation of the t-butylated diarylaminobenzaldehyde moieties. Buchwald-Hartwig cross-coupling [13, 14] between the t-butylated aniline, corresponding t-butylated arylbromide and 2-(4-bromophenyl)-1,3-dioxolane provided the t-butylated diarylamino-benzaldehydes in moderate yield. The dioxolane protecting groups were removed efficiently by column chromatography using silica-gel. In particular, this study revealed that the various diarylaminobenzaldehyde derivatives with bulky t-butyl substituents could be prepared efficiently using a Buchwald-Hartwig cross-coupling reaction. Finally, Knoevenagel condensation [15] between the corresponding aldehydes and (6,8-di-tert-butyl-2-methyl-4H-chromen-4-ylidene)malononitrile provided the red emitters



Scheme 1. Synthesis and structures of red emitters **(3a-3d).**

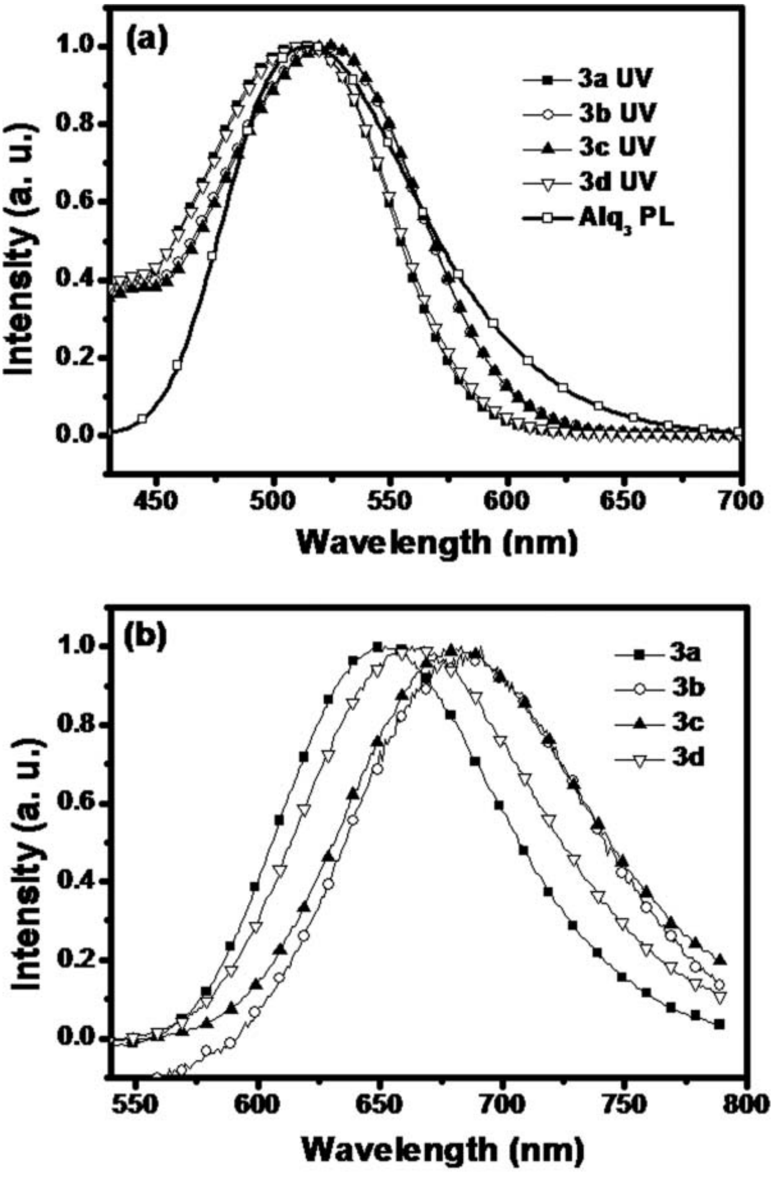


Figure 1. (a) UV-Vis spectra and (b) PL spectra of red emitters **3a**-**3d**.

3a-**3d** in moderate yield. These compounds were fully characterized by ^{1}H- and ^{13}C-NMR, FT-IR, and low- and high-resolution mass spectroscopy.

Figure 1 **(a)** presents the ultraviolet-visible (UV-Vis) absorption spectra of the red emitters **3a**-**3d**. The maximum absorption peaks of the red emitters **3a**-**3d** were 512, 522, 523, and 513 nm, respectively. Figure 1 **(a)** shows the good overlap between the emission spectra of a common host material, Alq$_3$, and the absorption spectra of the red emitters **3a**-**3d**. This suggests that Förster singlet energy transfer from the host Alq$_3$ to the red emitter **3a**-**3d** is efficient, and Alq$_3$ served well as a host in the OLEDs using

Table 1. Physical properties of red emitters **3a**-**3d**

Compound	UV_{max} (nm)[a]	PL_{max} (nm)[b]	FWHM	HOMO/ LUMO (eV)[b]	E_g	Q.Y[c]	mp(°C)
3a	512	652	108	5.50/3.36	2.14	0.40	176
3b	522	691	117	5.26/3.20	2.06	0.14	276
3c	523	683	115	5.36/3.26	2.10	0.25	280
3d	513	668	111	5.43/3.32	2.11	0.19	177

[a]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]Fluorescent quantum yields were determined in 1.2-dichloroethane at 293 K against DCJTB ($\Phi = 0.78$) [12].

compounds **3a**-**3d** as red dopant materials. Red emitters **3a**-**3d** exhibited efficient red emission with maximum emission peaks of 652, 691, 683, and 668 nm, respectively, as shown in Figure 1 **(b)**. Interestingly, among the red emitters **3a**-**3d**, **3a** showed the shortest maximum emission peak. The severe steric hindrance between the 2-fluorenyl group and phenyl groups in (2-fluorenyl)(phenyl)aminophenyl moiety of compound **3a** induced large angle distortion of (2-fluorenene)-N-(benzene), and reduced the orbital overlap between the lone-bonding electrons in the nitrogen atom and the π-conjugated styryl moiety of compound **3a**. Presumably, this reduced electron donating capability the lone-bonding electrons in nitrogen atom of compound **3a** would weaken the donor-acceptor interaction in compound **3a** and increase the energy band-gap of **3a** [16]. Their quantum yields were 0.40, 0.14, 0.25, and 0.19, respectively.

The HOMO (highest occupied molecular orbital) and LUMO (Lowest occupied molecular orbital) levels of the new Red emitters **3a**-**3d** were −5.26 to −5.50 eV and −3.20 to −3.26 eV, respectively. Table 1 lists the physical properties. Among the red emitters **3a**-**3d, 3a** appears to be an excellent candidate for the emitting material of red fluorescent OLEDs because it has a suitable maximum emission peak near the saturated red emission (~650 nm) and highest quantum yield (0.40). Therefore, an OLED device using compound

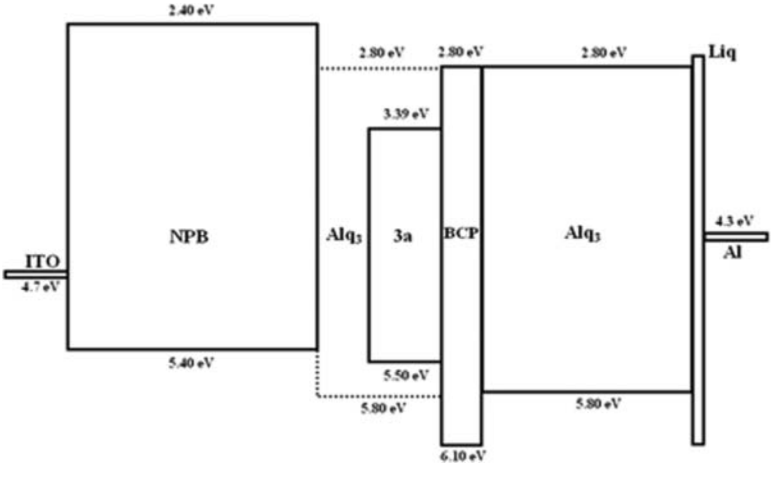


Figure 2. Structure and Energy-level diagram of device **1**.

Table 2. EL performance characteristic of device**s** **1** and **2**

Device	Dopant (doping%)	L(cd/m^2)[a]	LE-J(cd/A)[a]/[b]	PE-J(lm/W)[a]/[b]	CIE(x,y)[c]
1	3a (2%)	3357	1.12/0.94	0.60/0.37	(0.64,0.35)
2	DCCPA (2%)	203	0.81/0.76	0.30/0.21	(0.64,0.36)

[a]Maximum values. [b]Values at 20 mA/cm^2. [c]Values at 7.0 V.

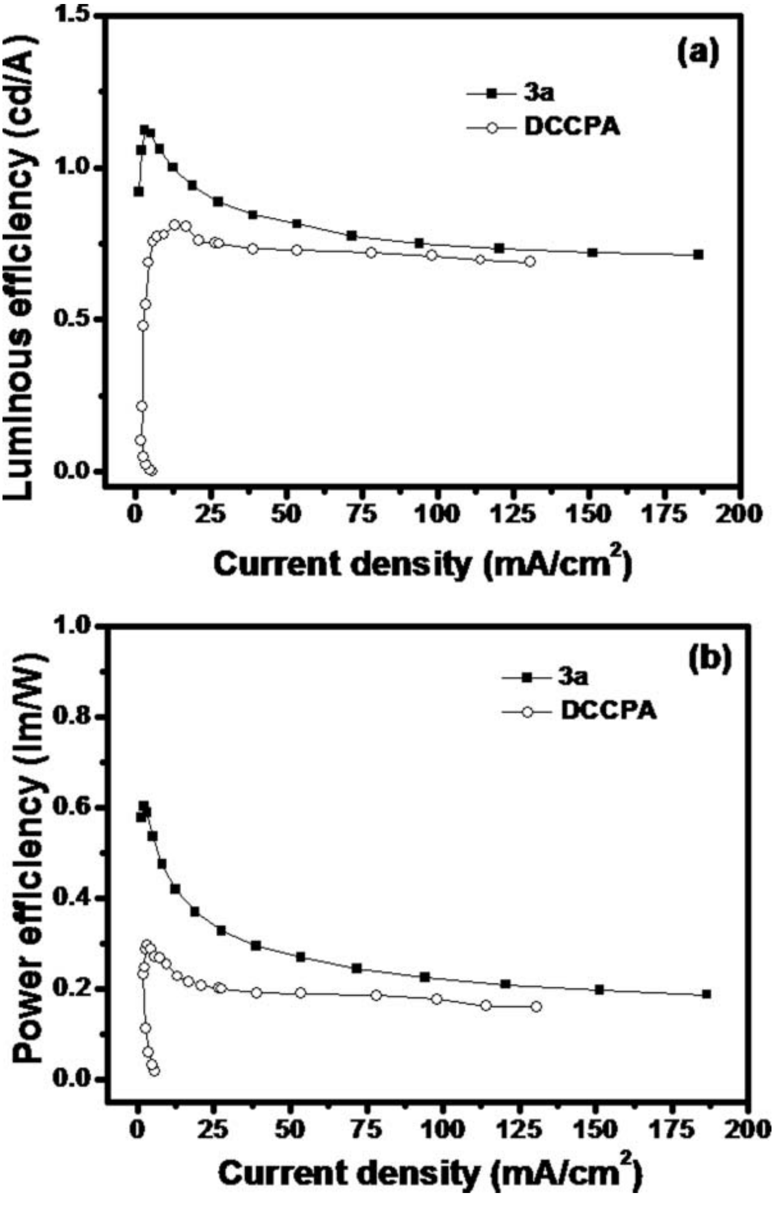


Figure 3. (a) Luminous efficiencies-current density and (b) Power efficiencies-current density characteristics of devices **1** and **2**.

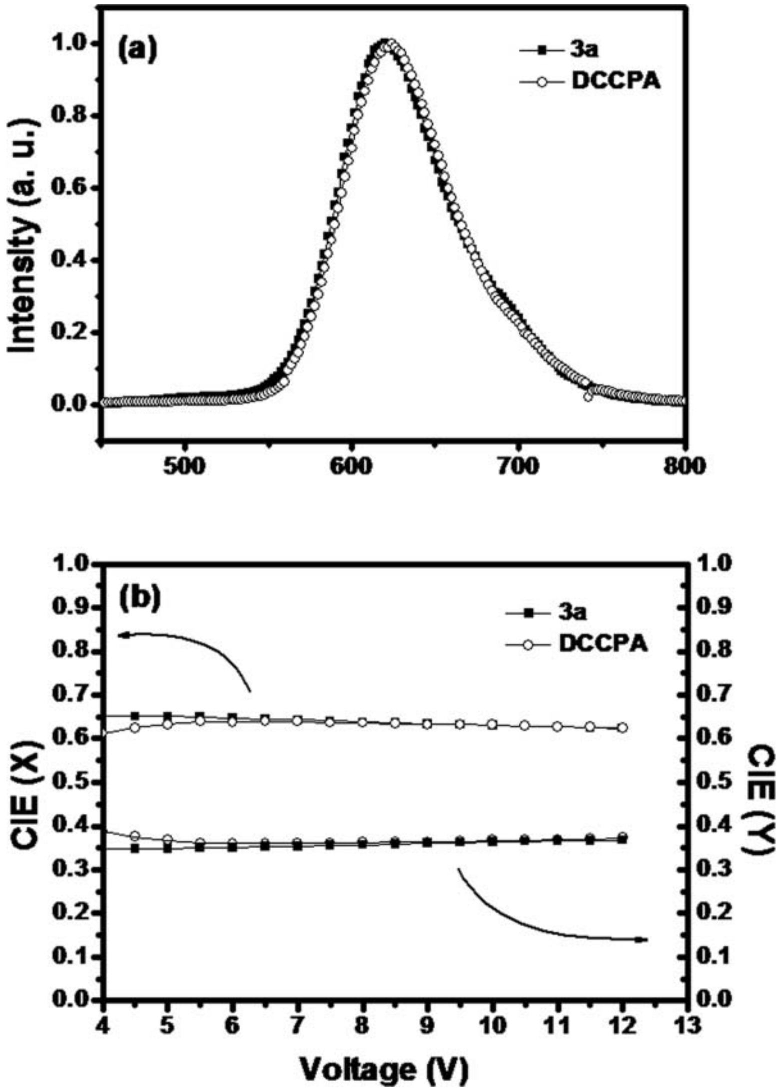


Figure 4. (a) EL spectra and (b) CIE coordinates of the devices **1** and **2**.

3a as a dopant in the Alq_3 host was fabricated, as shown in Figure 2. NPB, Alq_3, and Liq were used as the hole transporting layer, red host and electron transporting layer, and electron injection layer, respectively. In particular, BCP with a high HOMO energy level was used as a hole blocking material to improve the EL efficiency of the devices by blocking hole-leakage from the emitting layer to the electron transporting layer and confine the excitons to the emitting layer [17].

Table 2 summarizes the electroluminescent data of these devices with that of DCCPA. Figure 3 shows the luminous efficiency and power efficiency of device **1**. The maximum luminous efficiency and maximum power efficiency of device **1** was 1.12 cd/A and 0.60 lm/W, respectively. As shown in Table 2, compared to the device using DCCPA without any t-butyl groups as the dopant, a device using compound **3a** as a dopant showed superior

EL efficiency. Presumably, in device **1** using the red emitter **3a**, the bulky t-butyl groups of the red emitter **3a** would increase the steric hindrance between the red emitter **3a** in the emitting layer of the device, which would lead to improved EL performance by preventing concentration quenching [18].

Figure 4 presents the electroluminescent emission spectra and Commision Internationale De L'Eclairage ($CIE_{x,y}$) coordinates of device **1**. The maximum peak of the EL spectra was 620 nm, and the CIE coordinates were (0.64, 0.35), at 7.0 V. The device also showed stable color chromaticity at various voltages. Compared to a device using DCCPA, device **1** using **3a** showed much improved CIE coordinates.

Conclusions

New red emitters, t-butylated 2-(2-(4-(diarylamino)styryl)-4H-chromen-4-ylidene) malononitrile derivatives **3a-3d**, were designed and synthesized. A device with the following structure: ITO/NPB (50 nm)/Alq_3 : Red dopants **3a** (2%) (30 nm)/ BCP (10 nm)/Alq_3 (40 nm)/Liq (2 nm)/Al, was fabricated. This device showed the maximum luminous and power efficiencies of 1.12 cd/A and 0.60 lm/W, respectively. The CIE coordinates were (0.64, 0.35) at 7.0 V, and the device also showed stable color chromaticity with various voltages. Compared to a device using a non-t-butylated emitter, this device using a t-butylated emitter showed improved EL performance due to the reduced molecular aggregation and concentration quenching.

References

[1] Tang, C. W. and VanSlyke, S. A., *Appl. Phys. Lett.*, **51**, 913, (1987).
[2] Li, Z. and Meng, H. Eds. *Organic Light-Emitting Materials and Devices*, Taylor & Francis: Boca Raton, U. S. A. pp 295, (2007).
[3] Lee, K. H., Kwon, Y. S., Kang, L. K., Kim, G. Y., Seo, J. H., Kim, Y. K., and Yoon, S. S., *Synth. Met.*, **159**, 2603, (2009).
[4] Kwon, Y. S., Lee, K. H., Kim, G. Y., Seo, J. H., Kim, Y. K., and Yoon, S. S., *J. Nanosci. Nanotechnol.*, **9**, 7056, (2009).
[5] Kim, S. O., Lee, K. H., Kang, S., Lee, J. Y., Seo, J. H., Kim, Y. K., and Yoon, S. S., *Bull. Korean Chem. Soc.*, **31**, 389, (2010).
[6] Lee, K. H., Seo, J. H., Kim, Y. K., and Yoon, S. S., *J. Nanosci. Nanotechnol.*, **9**, 7099, (2009).
[7] Chen, C., *Chem. Mater.*, **16**, 4389, (2004).
[8] Chen, C. H., Tang, C. W., Shi, J., and Klubek, K. P., *Thin Solid Films.*, **363**, 327, (2000).
[9] Tang, C. W., Van Slyke, S. A., and Chen, C. H., *J. Appl. Phys.*, **65**, 3610, (1989).
[10] Zhang, X. H., Chen, B. J., Lin, X. Q., Wong, O. Y., and Lee, C. S., Kwong, H. L., and Lee, S. T., Wu, S. K., *Chem. Mater.*, **13**, 1565, (2001),
[11] Chen, B. J., Sun, X. W., Lin, X. Q., and Lee, C. S., Lee, S. T., *Mater Sci & Eng.*, **B100**, 59, (2003).
[12] Chen, C. H., Tang, C. W., Shi, J., and Klubek, K. P., *Macromol. Symp.*, **125**, 49, (1998).
[13] Wolfe, J. P., Wagaw, S., and Buchwald, S. L., *J. Am. Chem. Soc.*, **118**, 7215, (1996).
[14] Hartwig, J. F., *Acc. Chem. Res.*, **31**, 852, (1998)
[15] Jones, G., *Org. React.*, **15**, 204, (1967).
[16] Timothy, T. S. and Khalil, A. A., *Chem. Comm.*, **17**, 4904, (2007).
[17] Yeh, H., Chan, L., Wua, W., and Chen, C., *J. Mater. Chem.*, **14**, 1293, (2004).
[18] Kido, J., Hayase, H., and Hongawa, K., *Appl. Phys. Lett.*, **65**, 2124, (1994).