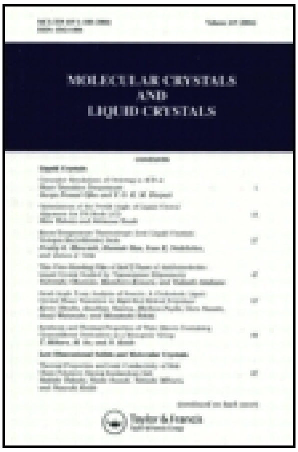

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Synthesis and Electroluminescent Properties of Red Fluorescent 2-(6,8-di-tert-butyl-2-(4-((3,5-di-tert-butylphenyl)(4-(trimethylsilyl)phenyl)amino)styryl)-4H-chromen-4-ylidene)malononitrile (DCCTBPA) for Organic Light-Emitting Diodes (OLEDs)

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Synthesis and Electroluminescent Properties of Red Fluorescent 2-(6,8-di-tert-butyl-2-(4-((3,5-di-tert-butylphenyl)(4-(trimethylsilyl)phenyl)amino)styryl)-4H-chromen-4-ylidene)malononitrile (DCCTBPA) for Organic Light-Emitting Diodes (OLEDs)

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We synthesize a red fluorescent material, 2-(6,8-di-tert-butyl-2-(4-((3,5-di-tert-butylphenyl)(4-(trimethylsilyl)phenyl)amino)styryl)-4H-chromen-4-ylidene)malononitrile (DCCTBPA) using Knoevenagel condensation. To explore the electroluminescent properties of materials multilayered OLEDs were fabricated by employing DCCTBPA as a dopant material. This device showed the luminous and power efficiencies of 0.73 cd/A and 0.31 lm/W at 20 mA/cm^2, respectively, with the CIE coordinates of (0.66, 0.34) at 7.0 V. Compared to a device using DCCPA, this device using DCCTBPA showed the improved EL performances due to reducing the molecular aggregation and thus preventing concentration quenching.

Keywords Chromene Derivatives; OLED; Red Fluorescence; t-Butyl group

Introduction

Many research efforts have been focused on the development of the emitting materials for organic light-emitting diodes (OLEDs) due to their potential application in flat panel displays and solid-state lighting [1,2]. Among the blue-, green-, and red-light-emitting materials required for full-color displays, red-light-emitting mater-ials remain one of the greatest challenges because of the lack of high-performance [3] Presently, most high-performance red OLEDs are made by doping a red dye into a suitable host [4]. The most widely studied dopants are pyran-containing compounds such as DCM and DCJTB have been widely studied [5,6], but their EL performances are not pleased with a prerequisite for the practical applications. Recently, Lee et al. group reported a new red fluorescent material based on chromene moiety such as 2-(2-(4-(diphenyl-amino)styryl)-4H-chromen-4-ylidene) malono-nitrile (DCCPA), and showed the red electro-luminescence with the power efficiency of 0.139 lm/W and the CIE coordinate of (0.60, 0.39) in an OLED device using this materials as a dopant. Furthermore, a derivative of DCCPA such as 2-(2-(4-(diphenyl-amino)styryl)-4H-6,7-dimethyl-chromen-4-ylidene)malononitrile (DCCMPA) has showed

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the improved EL performance due to the introduction of two methyl substituents on the chromene moiety by preventing concentration quenching [7,8].

In this paper, we describe the synthesis and electroluminescent properties of a red fluore-scent material, 2-(6,8-di-tert-butyl-2-(4-((3,5-di-tert-butylphenyl)(4-(trimethylsilyl) phenyl) amino)styryl)-4H-chromen-4-ylidene)malononitrile (DCCTBPA). In red emitter DCCTBPA, the bulky t-butyl groups and trimethylsilyl group are introduced into DCCPA skeleton to increase steric hindrance between red emitters in the emitting layer of devices and thus improve the EL performances by preventing concentration quenching.

Experimental

Materials and Measurement

All commercially available reagents were purchased from Aldrich and TCI and used without further purification. ^{1}H- and ^{13}C-NMR were recorded on a Varian (Unity Inova 300Nb) spectrometer. FT-IR spectra were recorded using a Thermo Nicolet Avatar 320 FT-IR 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 $= 0.78$ [16]. The HOMO energy levels were measured with low energy photo-electron spectrometry (Riken-Keiki AC-2). The LUMO energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

Synthesis

Synthesis of 6,8-di-tert-butyl-2-methyl-4H-chromen-4-ylidene)malononitrile (1). 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, acetyl chloride (2.01 mmol) was added at room temperature. After stirred for 1 h, NH_4Cl was added at 0°C. The solution was extracted with hexane and brine. The resulting materials were dissolved in glacial acetic acid (5 ml) and HCl (1 ml) and then were heated to 100°C for 1 h. After cooling to room tem-perature, the reaction mixture was washed to $NaHCO_3$ and extracted with ethyl acetate and brine. After filtration and evaporation of solvent, 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 for 24 h. The solution was washed to $NaHCO_3$ and extracted with CH_2Cl_2. After filtration and evaporation of solvent, the mixture was purified by re-crystallized with CH_2Cl_2 and hexane. (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; Mass (EI) *m/z* $= 320$ (M^{+}).

Synthesis of 4-((3,5-di-tert-butylphenyl)-(4-(trimethylsilyl)phenyl)amino)benzaldehyde (2). 3,5-di-tert-butylaniline(2.43 mmol) and 2-(4-bromophenyl)-1,3-dioxolane (2.43 mmol) were dissolved in toluene (7 ml). Pd_2dba_3 (0.12 mmol), NaOt-Bu (7.29 mmol), and 2-P(t-bu)$_2$biphenyl (0.24 mmol) were then added. The reaction mixture was heated to 80°C for 5 h, and then 1-bromo-4-trimethylsilyl benzene (2.43 mmol) was added and heated to 80°C for 24 h. The solution was extracted with ethyl ether and brine. The combined organic layers were washed with brine and $MgSO_4$. After filtration and evaporation of solvent, the mixture was purified by silica gel column chromatography with ethyl acetate and hexane. The obtained compound was yellowish solid (Yield : 29%). The obtained compound was yellowish solid. (Yield : 23%) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.52, (s, 1H), 7.39 (d, J = 8.9 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.99 (m, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.75 (m, 4H), 0.99 (s, 18H) 0.01 (m, 9H); ^{13}C-NMR (500 MHz): δ 152.1, 146.6, 134.8, 131.5, 127.6, 125.0, 123.6, 122.3, 121.6, 120.5, 119.2, 118.0, 65.6, 35.2, 31.7, 0.9; Mass (EI) m/z = 457 (M^+).

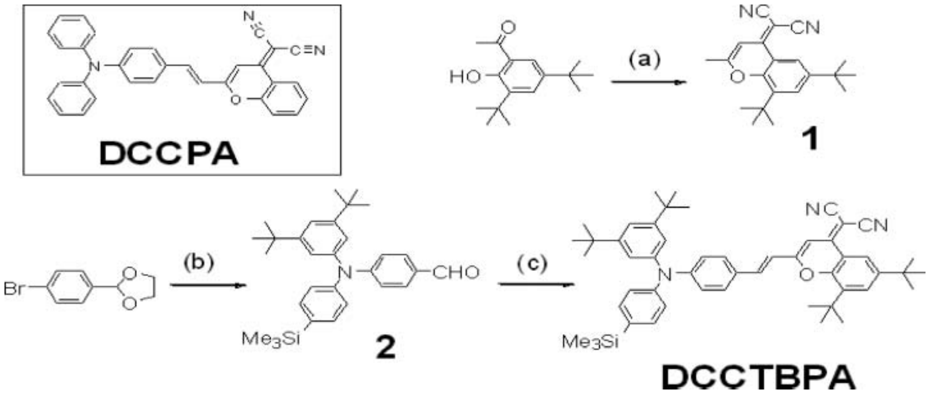
Synthesis of DCCTBPA. Compound **1** (1.09 mmol) and Compound **2** (1.09 mmol) into RBF were added and connected with deanstark trap (put the molecular sieve), reflux condenser. And then anhydrous ethyl alcohol (30ml), piperidine (4.91 mmol) were added and heated to 95°C for 5 h and then cooled to room temperature. The mixture was filtered and extracted with ethyl acetate and brine. After filtration and evaporation of solvent, the mixture was purified by re-crystallized with ethyl alcohol. (Yield : 78%) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.43 (d, J = 9.0 Hz, 1H), 7.22 (d, J = 6.6, 1.9 Hz, 1H), 7.10 (d, J = 8.5 Hz, 4H), 7.02 (t, J = 1.6 Hz, 1H), 6.93 (m, 4H), 6.80 (m, 5H), 1.03 (s, 10H), 1.01 (s, 22H), 0.04 (s, 3H), 0.01 (s, 10H); ^{13}C-NMR (500 MHz): δ 212.6, 203.7, 190.5, 170.4, 167.3, 153.2, 152.3, 149.8, 149.4, 135.0, 131.0, 128.3, 124.6, 124.2, 123.0, 121.2, 121.1, 118.7, 118.4, 106.3, 104.8, 66.3, 36.4, 35.8, 32.3, 32.2, 31.0, 21.4, 0.9; FT-IR (KBr): ν = 2978, 2341, 1590, 1556, 1505, 1492, 1320, 835 cm^{-1}; Mass (EI) m/z = 759 (M^+); HRMS (EI) calcd for $C_{51}H_{61}N_3OSi$, 759.4584; found, 759.4589; mp. 151°C.

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. The device structures were as follows: (1) ITO/*N*,*N*′-diphenyl-*N*,*N*′-(1-napthyl) -(1,1′-biphenyl)-4,4′-diamine (NPB) (50 nm)/ tris(8-quionlinolato)-aluminium (Alq_3): Red dopant (1 or 2%) (30 nm)/Alq_3 (5 nm)/Liq (2 nm)/Al. (2) ITO/NPB (50 nm)/Alq_3: Red dopant (2%) (30 nm)/bathucuproine (BCP) (10 nm)/ Alq_3 (40 nm)/Liq (2 nm)/Al. All of the pro-perties of the OLEDs such as the current density (*J*), luminance (*L*), luminance efficiency (LE), power efficiency (PE), and commission inter-national de 1′Éclairage (CIE) coordinate charac-teristics 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

Structure and synthetic scheme of DCCTBPA were shown in Scheme 1. The UV-Vis absorption and PL spectra of DCCTBPA and DCCPA are shown in Fig. 1. In particular, Fig. 1(a) shows the good overlap between the emission spectra of a common host material Alq_3, and the absorption spectra of DCCTBPA and DCCPA. This observation imply that the Förster singlet energy transfer from host Alq_3 to red emitter DCCTBPA and DCCPA would be efficient, and Alq_3 served well as a host in the OLEDs by using these compounds as red dopant materials. Red emitters DCCTBPA and DCCPA exhibit efficient red emissions with maximum emission peaks of 663 and 650 nm, respectively, as shown in Fig. 1 (b). Inter-estingly, red emitter DCCTBPA has the longer maximum emission peak than DCCPA. The electron-donating t-butyl and trimethylsilyl groups in diaryl-aminophenyl moiety of



Scheme 1. Synthesis and structures of the red materials DCCTBPA. **a)** i) NaH, AcCl, ii) HCl, AcOH, iii) Malonitrile, Ac_2O, **b)** 1-bromo-4-trimethysilylbenzene, 3,5-di-tertButylaniline, Pd_2dba_3, 2-(di-tert-butylphosphino)-biphenyl, Na-O-(t-Bu), **c) 1**, Piperidine, EtOH.

DCCT-BPA increase the electron density around nitro-gen atom of DCCTBPA and thus improve the donor-acceptor interaction in DCCTBPA. Pre-sumably, this would make the energy band-gap of DCCTBPA narrower than that of DCCPA[9]. All physical properties were shown in Table 1.

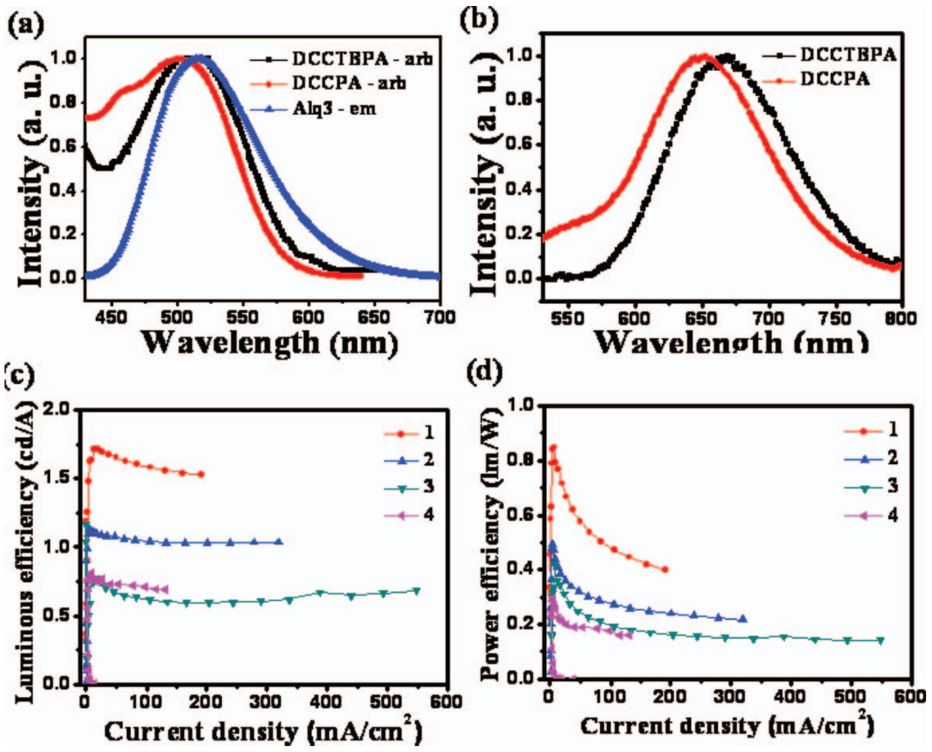


Figure 1. (a) UV-Vis spectra and (b) PL spectra of red emitters **DCCTBPA** and **DCCPA.** (c) Luminous efficiencies-current density and (d) Power efficiencies-current density characteristics of devices **1–4**.

Table 1. Physical properties of red emitters DCCTBPA and DCCPA

Compound	UV_{Max} (nm)[a]	PL_{Max} (nm)[a]	FWHM	HOMO (eV)[b]	LUMO (eV)[b]	Eg	Q.Y[c]
DCCTBPA	513	663	103	5.63	3.54	2.09	0.40
DCCPA	502	650	105	5.60	3.45	2.15	0.54

[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] Using DCJTB as a standard; $l_{ex} = 550$ nm ($\Phi = 0.78$ in 1,2-dichloroethene).

To explore the electroluminescent properties of DCCTBPA, OLED devices using DCCTBPA as a dopant in Alq_3 host were fabricated. Particularly, to optimize the device structure, two kind of devices with or without BCP were fabricated. BCP with the high HOMO energy level was used as hole blocking material to improve the EL efficiencies of devices by blocking hole-leakage from the emitting layer to the electron transporting layer and thus the con-finement of excitons in the emitting layer [10]. Also, for the comparison, the control device using DCCPA as a dopant in Alq_3 host was fabricated. All electroluminescent data on devices using DCCTBPA and DCCPA was summarized in Table 2. The luminous and power efficiencies of devices are shown in Figure 1 (c) and (d), respectively. Also, the EL spectra of devices are shown in Figure 2. In devices 1 and 2 using DCCTBPA, with the increase of doping percentage of dopants, the luminous and power efficiencies decreased due to the concentration quenching effect. The EL spectra of devices **1** and **2** showed Alq_3 emissions around 510 nm due to the exciton leakages from emitting layer to Alq_3 in the electron transporting layer. Also, the EL spectrum of device **2** showed the shoulder peak around 700 nm, which originated from the excimers of dopant DCCTBPA. Thus the CIE coordinates of devices **1** and **2** are in the yellow-orange not the red region. Interestingly, compared to device **2** without BCP layer, the EL spectrum of device **3** with BCP layer showed no Alq_3 emission due to the blocking hole leakages from emitting layer to Alq_3 in the electron transporting layer. Thus, compared to device **2**, device **3** had the improved CIE coordinates of (0.66, 0.34) at 7.0 V, approaching saturated red emission. The luminous and power efficiencies of the device **3** were 0.73 cd/A and 0.31 lm/W at 20 mA/cm^2, respectively. Notably, compared to device **4** using DCCPA as a dopant, the power efficiency of device **3** using **DCCTBPA** as a dopant increased by 48% at 20 mA/cm^2. The bulky t-butyl groups and trimethylsilylmethyl group of dopant **DCCTBPA** could prevent molecular aggregation and thus reduce concentration quenching. This would contribute to the improved luminous

Table 2. EL performance characteristic of devices DCCTBPA and DCCPA

Device	Dopant (doping%)	L[a] (cd/m^2)	LE-J[a]/[b] (cd/A)	PE-J[a]/[b] (lm/W)	CIE[c] (*x*,*y*)
1	DCCTBPA(1%)	2928	1.71/1.71	0.72/0.85	(0.50,0.44)
2	DCCTBPA(2%)	1096	1.10/1.13	0.38/0.49	(0.51,0.44)
3	DCCTBPA(2%—BCP)	1465	0.73/0.80	0.31/0.42	(0.66,0.34)
4	DCCPA(2%—BCP)	203.4	0.76/0.81	0.21/0.30	(0.64,0.36)

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

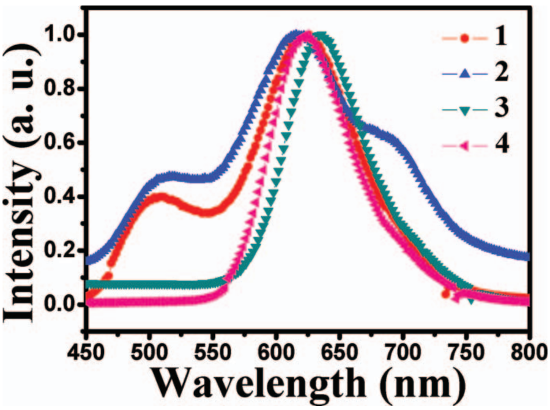


Figure 2. EL spectra the devices **1 – 4**

efficiency of device **3** [11,12]. Furthermore, compared to device **4** with the CIE coordinate of (0.64, 0.36), device **3** had the improved CIE coordinate of (0.66, 0.34) at 7.0 V, which might be originated from the electron-donating effects of t-butyl and trimethylsilyl groups of DCCTBPA dopant in device **3**.

Conclusions

We designed and synthesized new red emitter DCCTBPA based on 2-(2-(4-(diarylamino) styryl)-4H-chromen-4-ylidene)malononitrile (DCCPA) skeleton. A device with the structure of ITO/NPB (50 nm)/Alq_3 : DCCTBPA (2%) (30 nm)/ BCP (10 nm)/Alq_3 (40 nm)/Liq (2 nm)/Al showed the luminous and power efficiencies of 0.73 cd/A and 0.31 lm/W at 20 mA/cm^2, respectively. The CIE coordinates of this device was (0.66, 0.34) at 7.0 V, approaching saturated red emission with the CIE coordinate of (0.67, 0.32). Compared to a device using DCCPA, this device using DCCTBPA showed the improved EL performances due to reducing the molecular aggregation and thus preventing concentration quenching. This study demonstrates that a DCCPA derivative, DCCTBPA possesses excellent properties for efficient red fluorescent OLEDs.

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