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Red Fluorescent Organic Light-Emitting Diodes (OLEDs) using 4-(1,3-Indanedione-2-yl)-2-(adaman-1-yl)-6-(10-aza-2,3,4,5,6,7-hexahydronaphtio[1,8-gh]chromen-10(1H)-one-9-enyl)-4H-pyran

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Red Fluorescent Organic Light-Emitting Diodes (OLEDs) using 4-(1,3-Indanedione-2-yl)-2-(adamantan-1-yl)-6-(10-aza-2,3,4,5,6,7-hexahydronaphtho[1,8-gh]chromen-10(1H)-one-9-enyl)-4H-pyran

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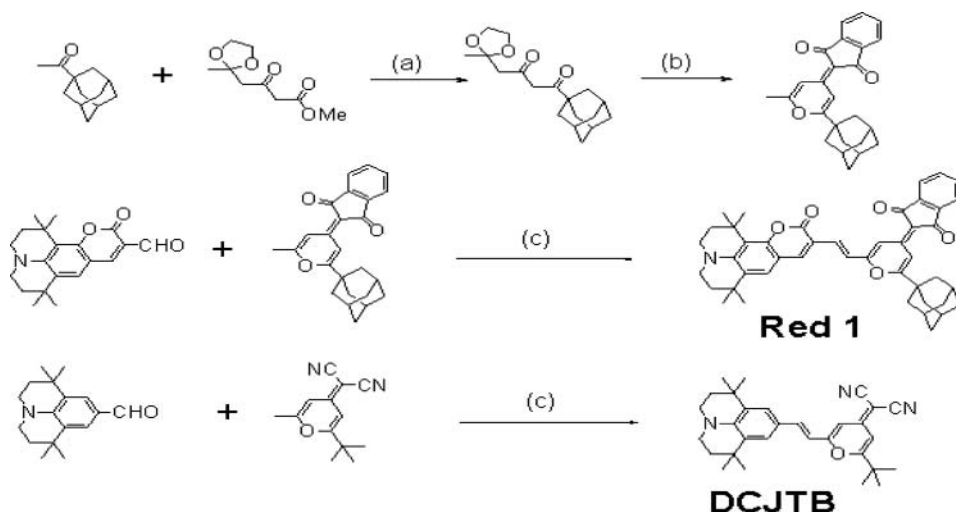
A red fluorescent material 4-(1,3-Indanedione-2-yl)-2-(adamantan-1-yl)-6-(10-aza-2,3,4,5,6,7-hexahydronaphtho[1,8-gh]chromen-10(1H)-one-9-enyl)-4H-pyran is synthesized and characterized. In this material, four methyl groups and adamantly group are introduced into DCJTb skeleton to increase steric hindrance between red emitters in the emitting layer of devices and thus improve the EL efficiencies by preventing concentration quenching. In particular, a device doped with this material in the emitting layer exhibits the luminous and power efficiencies of 3.58 cd/A and 1.61 lm/W at 20 mA/cm², respectively. The CIE coordinates of this device was (0.64, 0.35) at 7.0V.

Keywords Red Fluorescence; OLEDs; DCJTb derivative; Adamandane; Indanedione group

Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention due to their potential application in flat panel displays [1]. Among three elemental colors of red, green and blue for full color display applications, red fluorescent materials are far behind in terms of efficiency and color purity [2]. The well-known pyran-containing laser dyes based on DCM (4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran) have been widely studied [3,4]. In most DCM type emitters, dramatically reduces EL performance due to concentration quenching. Thus, there had been considerable efforts to developed efficient red fluorescent materials by preventing excimer and exciplex formation through incorporation of sterically bulky moieties in the emitters [5]. Particularly, 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTb) represents the most efficient fluorescent red emitting material for OLEDs [6]. In these material, the bulky substituents on julolidine and pyran moieties of DCM backbone are incorporated to prevent concentration quenching between the emitting materials, which lead to the improved EL efficiencies of devices [7].

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Scheme 1. Synthesis and structures of **Red 1** and **DCJTB**. (a) $\text{NaN}(\text{TMS})_2$. (b) i. H_2SO_4 , ii. 1,3-Indanedione, Ac_2O . (c) Piperidine, EtOH .

Nevertheless, their EL performances still need to be improved. Particularly, color purities of devices using DCJTB is far from ideal [8]. This imply that the more bulky groups than tert-butyl group in DCJTB is need to improve the EL performances of red fluorescent OLEDs [9].

In this paper, we describe the synthesis and electroluminescent properties of a red fluorescent material, 4-(1,3-Indanedione-2-yl)-2-(adaman-1-yl)-6-(10-aza-2,3,4,5,6,7-hexahydronaphthio[1,8-*gh*]chromen-10(1*H*)-one-9-enyl)-4H-pyran (**Red 1**). In **Red 1**, four methyl groups and adamantly group are introduced into DCJTB skeleton to increase steric hindrance between red emitters in the emitting layer of devices and thus improve the EL efficiencies by preventing concentration quenching. Furthermore, the additional π conjugation groups such as pyran-2-one and 1,3-indanedione are incorporated to increase the $p \pi$ -conjugation length and thus improve the color purity of devices using **Red 1** [10–12].

Experimental

Materials and Measurement

All commercially available reagents were purchased from Aldrich and TCI and used without further purification. ^1H - and ^{13}C -NMR were recorded on a Varian (300 or Unity Inova 300Nb or Unity Inova 500Nb) 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 [13]. 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

Synthesis of 2-methyl-6-(adamantly-1-yl)-4-(1,3-indanedione-2-yl)-4H-pyran. To a solution of 2.6 g of 1-acetyl-adamantane (14.68 mmol) in 30 mL of THF at -78°C was added 36.71 mL of 1M $\text{NaN}(\text{TMS})_2$ solution in THF. After stirring 1 hr at -78°C , 4.7 g of methyl 2-(2-methyl-1,3-dioxolan-2-yl)acetate (29.37 mmol) was added and then heated to 70°C for 12 hr. The reaction mixture was quenched with NH_4Cl aqueous solution and then extracted with ethyl acetate. Column chromatography using silica gel with the elution of ethyl acetate and hexane provided 2.2 g of the crude 1-(adamant-1-yl)-4-(2-methyl-1,3-dioxolan-2-yl)butane-1,3-dione (7.22 mmol, 49.2%). This crude compound was dissolved in 10 mL of 95% H_2SO_4 solution and then stirred for 4 hr at room temperature. After the neutralization with NaHCO_3 solution, the reaction mixture was extracted with ethyl acetate. Without further purification, the crude products were dissolved in 10 mL of acetylanhydride and then 0.5 g of 1, 3-indanedione (3.12 mmol) was added to the reaction mixture. After refluxing the reaction mixture for 12 hr, the crude products were extracted with ethyl acetate. Column chromatography using silica gel with the elution of ethyl acetate and hexane provided 1.7 g of 2-methyl-6-(adamantly-1-yl)-4-(1,3-indanedione-2-yl)-4H-pyran (4.50 mmol, 62.3%). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 5.31 (s, 1H), 5.20 (s, 1H), 1.77 (s, 3H), 1.52 (m, 6H), 1.31 (m, 6H), 1.18 (t, 2H, $J = 7.5$ Hz), 1.10 (m, 6H), 0.91 (t, 3H, $J = 7.5$ Hz); FT-IR (KBr): $\nu = 2925, 2323, 1587, 1520, 830\text{ cm}^{-1}$; Mass (EI) $m/z = 336$ (M^+).

Synthesis of Red 1 (4-(1,3-Indanedione-2-yl)-2-(adaman-1-yl)-6-(10-aza-2,3,4,5,6,7-hexahydronaphtio[1,8-gh]chromen-10(1H)-one-9-enyl)-4H-pyran). To a solution of 0.68 g of 6-(10-aza-2,3,4,5,6,7-hexahydronaphtio[1,8-gh]chromen-10(1H)-one)-9-carboaldehyde (2.11 mmol) and 0.79 g of 2-methyl-6-(adamantly-1-yl)-4-(1,3-indanedione-2-yl)-4H-pyran (2.11 mmol) in 20 mL of EtOH was added 0.83 mL of piperidine (8.44 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 from ethyl alcohol provided 0.47 g of **Red 1** as reddish solids (0.686 mmol, 32.5%). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 7.61 (s, 1H), 7.42 (s, 1H), 6.65 (d, 1H, $J = 12.1$ Hz), 6.43 (d, 1H, $J = 12.0$ Hz), 5.45 (s, 1H), 5.15 (s, 1H), 3.45 (m, 2H), 3.23 (m, 2H), 1.91 (m, 2H), 1.45 (m, 12H), 1.31 (m, 12H), 1.21 (s, 6H), 1.11 (t, 2H, $J = 7.5$ Hz), 1.02 (s, 6H), 0.91 (t, 3H, $J = 7.5$ Hz); FT-IR (KBr): $\nu = 2989, 2330, 1582, 1559, 1500\text{ cm}^{-1}$; Mass

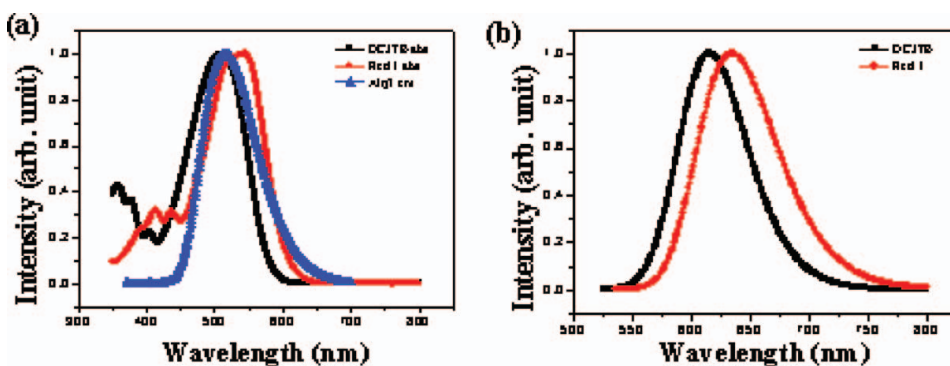


Figure 1. (a) UV-Vis absorption spectra and (b) Photoluminescence spectra of **Red 1** and DCJTb.

Table 1. Optical properties of **Red 1** and DCJTB

Compound	$\lambda_{\max}^{[a]}$ [nm]	$\lambda_{\max}^{[b]}$ [nm]	FWHM [nm]	HOMO/ LUMO[eV]	E_g	$\Phi^{[c]}$
1	542	633	80	−5.18/−3.09	2.09	0.71
DCJTB	511	620	72	−5.26/−3.10	2.16	0.78

^[a]Maximum absorption and emission wavelength, measured in $\text{Cl}_2\text{CH}_2\text{CH}_2\text{Cl}_2$ solution. ^[b] Obtained from AC-2 and absorption measurement. ^[c]Using DCJTB as a standard; $\lambda_{\text{ex}} = 500 \text{ nm}$ ($\Phi_p = 0.78$ in $\text{Cl}_2\text{CH}_2\text{CH}_2\text{Cl}_2$).

(EI) $m/z = 604$ (M^+); HRMS (EI) calcd for $\text{C}_{41}\text{H}_{53}\text{N}_3\text{O}$, 603.4189; found, 603.4178; mp, 258°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-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) (40 nm)/ tris(8-quinolinolato)-aluminium (Alq_3) : Red dopant (1, 5 or 10%) (20 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 l'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

Synthesis of the red emitter **Red 1** began with the preparation of two intermediates by following the known procedure [14]. **DCJTB** was prepared by following the standard procedure [15]. The ultraviolet-visible (UV-Vis) absorption spectra of **Red 1** and **DCJTB** are shown in Figure 1 (a). The maximum absorption peaks of these materials were 542 and 511 nm, respectively. Figure 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

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

Device	Dopant (doping%)	$L^{[a]}$ (cd/m^2)	$V_{\text{on}}^{[b]}$ (V)	LE- $J^{[c]/[d]}$ (cd/A)	PE $^{[c]/[d]}$ (lm/W)	EL $^{[e]}$ (nm)	CIE $^{[e]}$ (x, y)
1	Red 1(1)	10700	4.0	3.58/3.61	1.61/1.71	648	(0.64, 0.35)
2	Red 1 (5)	2000	5.0	0.54/0.56	0.15/0.29	656	(0.66, 0.33)
3	Red 1 (10)	340	6.0	0.13/0.15	0.03/0.07	672	(0.67, 0.32)
4	DCJTB (1)	6300	3.0	2.45/2.52	1.06/1.32	616	(0.60, 0.39)

^[a]Maximum luminance at 21.0 V, ^[b]Turn-on voltage at 1 cd/m^2 , ^[c]Value measured at 20 mA/cm^2 , ^[d]Maximum values, ^[e]Value measured at 7.0 V.

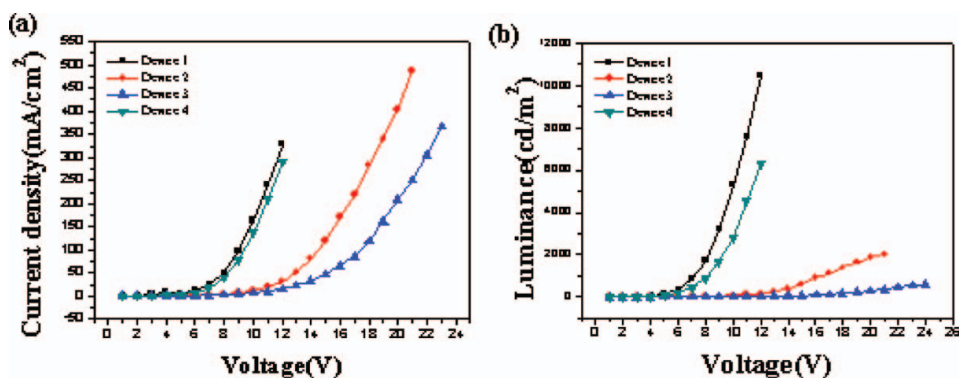


Figure 2. (a) Current density-Voltage and (b) Luminance-Voltage characteristics of devices 1–4.

DCJTB. This observation imply that the Förster Singlet energy transfer from host Alq₃ to red emitter **Red 1** and **DCJTB** would be efficient. **Red 1** and **DCJTB** exhibit efficient red emissions with maximum emission peaks of 633 and 620 nm, respectively, as shown in Figure 1 (b). Compared to **DCJTB**, the maximum emission peak of **Red 1** was red-shifted by 13 nm due to the increase the π -conjugation length of **Red 1**. The quantum yields of **Red 1** and **DCJTB** were 0.71 and 0.78, respectively in Table 1.

To explore the electroluminescent properties of **Red 1**, OLED devices using **Red 1** as a dopant in Alq₃ host were fabricated. Particularly, to optimize the device structure, three kinds of devices with the different doping concentrations such as 1, 5 and 10% were fabricated. Also, for the comparison, the control device using **DCJTB** as a dopant in Alq₃ host at 1% doping concentration was fabricated. All electroluminescent data on devices using **Red 1** and **DCJTB** was summarized in Table 2.

Figure 2 showed the current density-voltage and the luminance-voltage characteristics of devices. The luminous and power efficiencies of devices are shown in Figure 3. Also, the EL spectra of devices are shown in Figure 4. The maximum luminous efficiency of devices 1 and 4 were 3.61 and 2.52 cd/A, respectively. And the maximum power efficiency of devices 1 and 4 were 1.71 and 1.32 lm/W, respectively. The power efficiency of devices 1 and 4 were 1.61 and 1.06 lm/W at 20 mA/cm², respectively.

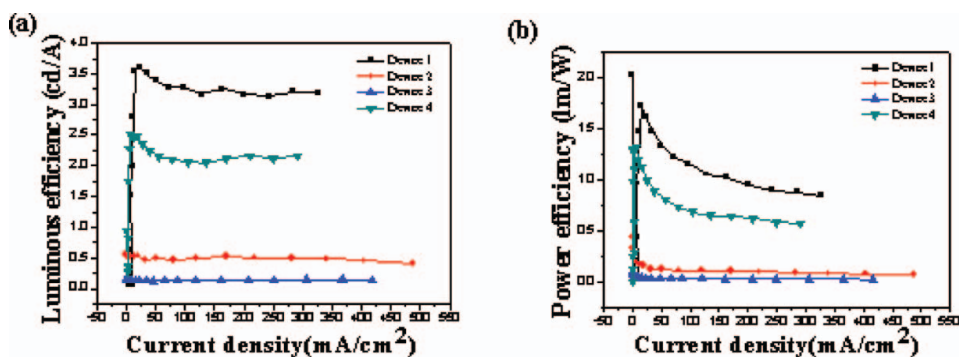


Figure 3. (a) Luminous efficiency-current density and (b) Power efficiencies-current density characteristics of devices 1–4.

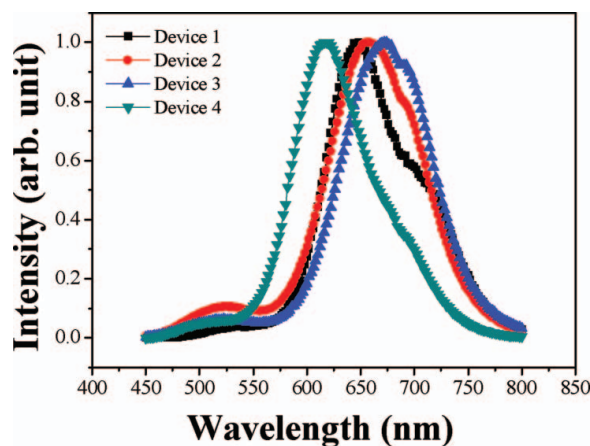


Figure 4. EL spectra devices of 1–4.

Notably, compared to device **4** using **DCJTB**, The methyl groups and adamantyl group of dopant **Red 1** of device **1** could prevent molecular aggregation and thus reduce concentration quenching [16]. This would contribute to the improved luminous efficiency of device **1**. Moreover, the other factor is such as the more effective hole trapping device **1** than device **4**. This implies that device **1** prevents hole leakage from emitting layer into Alq_3 layer. Thus more efficient exciton formation at device **1** could contribute to the improved EL efficiencies of device **1** in comparison to device **4** [17]. In devices **1**, **2** and **3** using **Red 1** as a dopant at the different doping concentrations, with the increase of doping concentration from 1% to 5 and 10%, the luminous and power efficiencies decreased due to the concentration quenching effect. Notably, the EL spectra of device **1**, **2** and **3** showed more red-shift by change of doping concentration. These observations imply that the emission peak around 670 nm might originate from the excimers of dopant **Red 1** and the extent of excimer formation of dopant increased at the higher doping concentration. Compared to device **4** with the CIE coordinates of (0.60, 0.39), device **1** has the improved CIE coordinates of (0.64, 0.35) due to the increase in the π -conjugation length of dopant [18]. Interestingly, compared to device **1**, device **2** and **3** showed the further improved CIE coordinates of (0.66, 0.33) and (0.67, 0.32) at 7.0 V, approaching saturated red emission due to the excimer formation of **Red 1** at the higher doping concentration. This study demonstrates that **Red 1**, a DCJTB derivative with modified julolidine and pyran moieties, is an excellent fluorescent red material for efficient OLEDs.

Conclusions

We designed and synthesized a new red emitter **Red 1** (4-(1,3-Indanedione-2-yl)-2-(adamant-1-yl)-6-(10-aza-2,3,4,5,6,7-hexahydronaphtho[1,8-*gh*]chromen-10(1*H*)-one-9-enyl)-4*H*-pyran). A device with **Red 1** (1%) showed the luminous and power efficiencies of 3.58 cd/A and 1.61 lm/W at 20 mA/cm², respectively. The CIE coordinates of this device were (0.64, 0.35) at 7.0 V. Compared to a device using **DCJTB**, this device showed the improved EL efficiencies due to prevent concentration quenching.

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