

Synthesis and Electroluminescent Properties of Julolidine- π -Julolidine Type Materials with the Bulky Adamantane Groups

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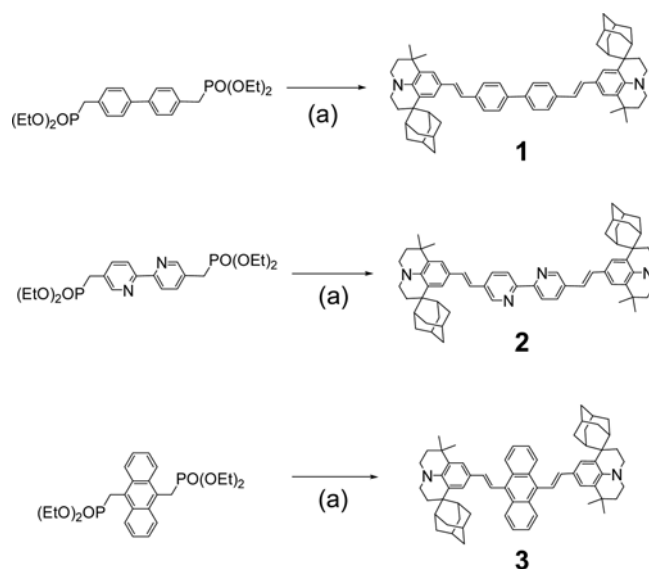
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For the application of organic light-emitting diodes (OLEDs) in full-color flat panel display and solid state lighting, the highly efficient emitting materials with the suitable color purities are needed.^{1,2} Among those, red fluorescent emitting materials remains one of the greatest challenges for the practical application of OLEDs.³⁻⁷ Recently, a variety of red fluorescent materials including the pyran containing materials, such as 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM), the arylamino-polyaromatic hydrocarbon derivatives, polyacenes and metal chelates have been widely studied.⁸

A main problem of red emitting material, which contributes to their low EL performances, is the concentration quenching due to the effective self aggregation and the consequent formation of excimers. To avoid this drawback and thus improve the EL properties of red fluorescent OLED devices, many synthetic efforts have been conducted to develop new emitting materials with the structural motifs to suppress self-aggregation by the weakening intermolecular attractive interactions. Particularly, the introduction of bulky moieties in the emitters would provide the steric hindrance between emitting materials in solid state devices and thus reduce the self-aggregation.⁹ Nevertheless, EL performances of red materials still need to be improved for the practical applications.

In this paper, we describe the synthesis and their electroluminescent properties of a series of donor-aromatic-donor type π -conjugated materials (**1-3**). In materials **1-3**, two donor moieties, (3,3-adamantyl-7,7-dimethyl)julolidine, were connected through three different aromatic groups such as biphenyl, 2,2'-bipyridine and anthracene, which have the different π -conjugation length and electronic properties. The change of aromatic backbone would lead the fine-tuning of emission wavelength of materials **1-3**. In donor moieties of materials **1-3**, the bulky adamantane groups are introduced to provide the steric hindrance during self-aggregation between emitting materials. This effect could suppress the formation of excimers of the emitting materials and lead the improved EL performances.

Synthesis of **1-3** began with the preparation of 5-(3,3-adamantyl-7,7-dimethyl)julolidine carboaldehyde by following the known procedure.¹⁰ Subsequently, Honor-Emmons reaction with the corresponding bis-phosphonates provided



Scheme 1. Synthesis and structures of **1-3**. (a) 5-(3,3-adamantyl-7,7-dimethyl)julolidine carboaldehyde, *t*-BuOK, THF.

materials **1-3** with the moderate yields, as shown in Scheme 1.

The ultraviolet-visible (UV-Vis) absorption spectra of **1-3** are shown in Figure 1. The maximum absorption peaks of these materials were 422, 441 and 459 nm, respectively. Compared to **1**, the maximum absorption peaks of **2** and **3** showed the red-shifts by 10 and 27 nm, respectively, due to the longer π -conjugation lengths. In **1**, the π -conjugation between two julolidine moieties is not effective due to the twisted structure of the central biphenyl moiety by the steric hindrances between two C-H of phenyl groups. However, these C-Hs of biphenyl moiety in **1** are replaced with nitrogen atoms in the central bipyridyl group of **2**. Thus, compared to **1**, **2** has the less twisted structure and the π -conjugation between two julolidine moieties of **2** is more effective. Also, compared **1** and **2**, the π -conjugation between two julolidine moieties of **3** is more effective due to the much more extended π -conjugated structure of anthracene moiety of **3** than the biphenyl and bipyridyl groups of **1** and **2**, respectively. In addition, Figure 1 shows the good overlap between the emission spectra of a common fluorescent host material 9,10-di-(2-naphthyl)anthracene (AND) and the absorption spectra of **1-3**. This observation imply that the

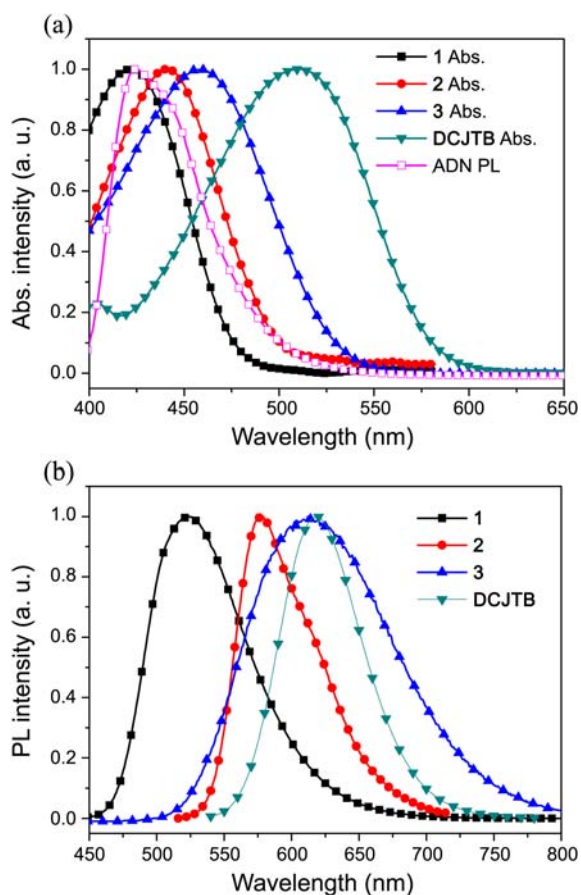


Figure 1. (a) UV-Vis and (b) PL spectra of emitters **1-3** and **DCJTJB**.

Förster singlet energy transfer from ADN to the emitters **1-3** would be efficient, and ADN served well as a host in the OLEDs by using these compounds as dopant materials. The emitters **1-3** exhibit the efficient emissions with maximum emission peaks of 524, 578 and 612 nm, respectively, as

shown in Figure 1(b), which depend on the π -conjugation lengths of **1-3**. The quantum yields of **1-3** were 0.39, 0.21 and 0.10, respectively. The HOMO/LUMO levels for **1-3** were $-5.35/-2.72$, $-5.36/-3.04$ and $-5.43/-3.09$ eV, respectively. All physical properties were shown in Table 1.

To explore the electroluminescent properties of **1-3**, OLED devices using **1-3** as dopants in ADN host were fabricated with the structure of ITO/*N,N'*-diphenyl-*N,N'*-(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) (50 nm)/9,10-di-(2-naphthyl)anthracene (ADN) : **1-3** (1 or 3%) (30 nm)/Alq₃ (40 nm)/LiQ (2 nm)/Al. NPB, ADN, Alq₃ and LiQ were used for hole transporting layer, host material in emitting layer, electron transporting layer, and electron injection layer, respectively. Also, for the comparison, the control device using a common red emitting material 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTJB) as a dopant in ADN host at 1% doping concentration was fabricated. All electroluminescent data on devices using **1-3** and **DCJTJB** were summarized in Table 2.

Figure 2 shows the EL spectra of devices **1-4**. The maximum peaks of EL spectra of devices **1-3** using the emitters **1-3** as dopants at the same 1% doping concentration were 527, 583 and 596 nm, respectively, which were well compatible with the trend of PL spectra of the emitters **1-3**. The CIE coordinates of devices **1, 2** and **3** were (0.32, 0.67), (0.45, 0.54) and (0.57, 0.42), respectively. Thus devices **1-3** emit the green, orange and orange-red region of the visible spectrum, which are all originated from emitters **1-3**, respectively. Notably, device **3** using emitter **3** showed the efficient orange-red emission, which is approaching close to that of device using a common red emitter DCJTJB. Interestingly, compared to device **3**, the EL spectra of device **4** with the higher doping concentration of **3** showed the red-shift by 23 nm, which might be originated from the excimers of dopant **3** in the emitting layer.

Figure 3 shows the current density-voltage and the lumin-

Table 1. Physical properties of emitters **1-3** and **DCJTJB**

Compound	UV _{max} ^a (nm)	PL _{max} ^a (nm)	FWHM	HOMO/LUMO (eV)	E _g	Q.Y. ^b
1	422	524	84	$-5.35/-2.72$	2.63	0.39
2	441	578	69	$-5.36/-3.04$	2.32	0.21
3	459	612	125	$-5.23/-2.89$	2.34	0.10
DCJTJB	511	619	72	$-5.26/-3.10$	2.16	0.78

^aMaximum absorption and emission wavelength, measured in 1,2-dichloroethane solution (1×10^{-5} M). ^bUsing DCJTJB as a standard; $\lambda_{\text{ex}} = 500$ nm ($\Phi_{\text{p}} = 0.78$ in 1,2-dichloroethane).¹¹

Table 2. EL performance characteristic of the doped-devices

Device	Dopant [x%] ^a	L ^b [cd/m ²]	LE ^c [cd/A]	PE ^c [lm/W]	EL ^d [nm]	CIE ^e (x, y)
1	1 [1]	9011	7.64	3.12	527	(0.32, 0.67)
2	2 [1]	3168	2.75	1.10	583	(0.45, 0.54)
3	3 [1]	4838	4.79	1.76	596	(0.57, 0.42)
4	3 [3]	1623	2.27	0.78	619	(0.61, 0.38)
5	DCJTJB [1]	3426	2.19	0.84	606	(0.59, 0.40)

^aDoping concentration. ^bMaximum luminance 12.0 V. ^cValues at 20 mA/cm². ^dValues at 7.0 V. ^eCommission Internationale de l'Enclairage (CIE) coordinates at 7.0 V.

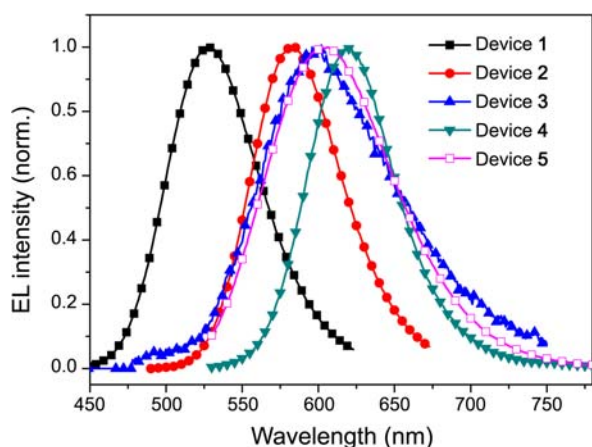


Figure 2. EL spectra the devices 1-5.

ance-voltage characteristics of devices. The luminous and power efficiencies of devices are shown in Figure 4. The luminous efficiency of devices 1, 2 and 3 using the emitters 1-3 as dopants at the same 1% doping concentration were 7.64, 2.75 and 4.79 cd/A at 20 mA/cm², respectively. And the power efficiency of devices 1, 2 and 3 were 3.12, 1.10 and 1.76 lm/W at 20 mA/cm², respectively. Among devices 1-3, device 1 showed the most efficient emission. Compared to emitters 2 and 3, the higher quantum yield of emitter 1 would partially contribute to the improved EL efficiencies of

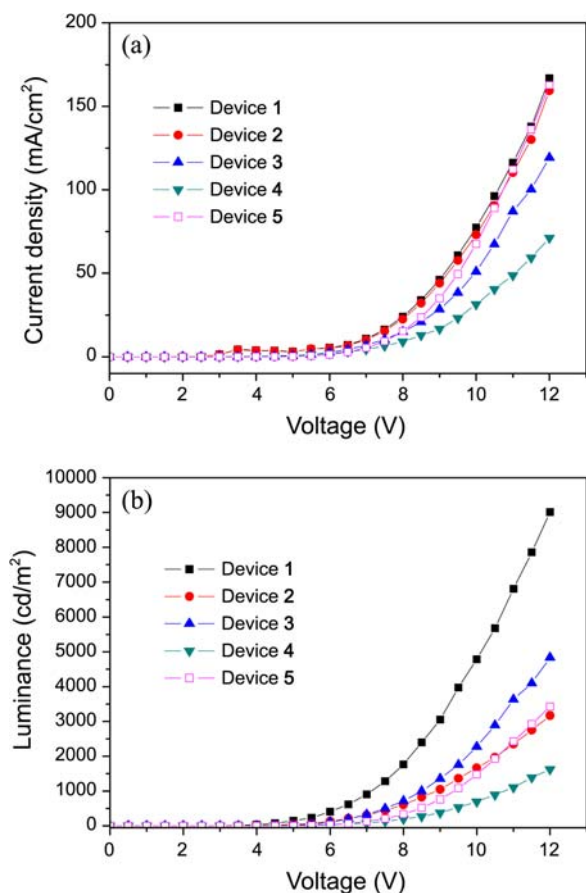


Figure 3. (a) Current density-voltage and (b) luminance-voltage characteristics of devices 1-5.

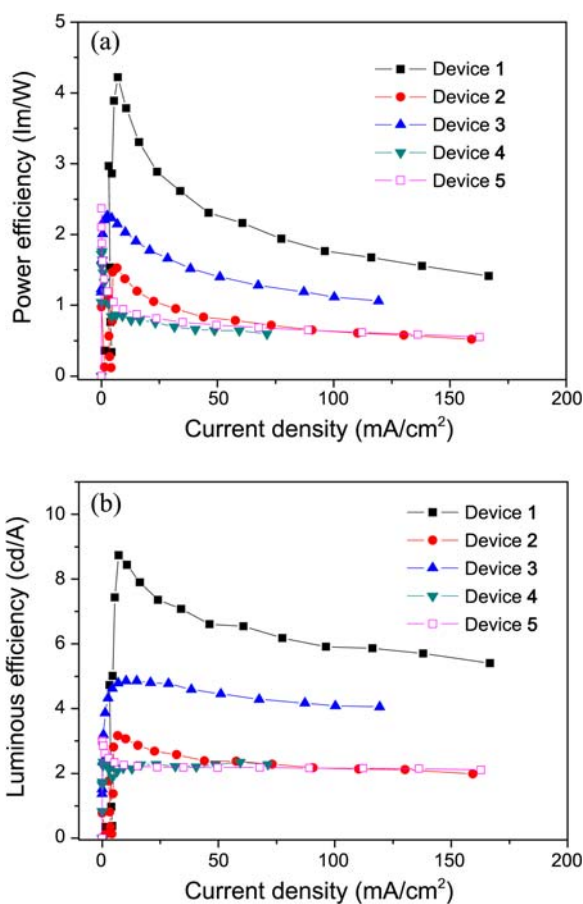


Figure 4. (a) Luminous efficiencies-current density and (b) power efficiencies-current density characteristics of devices 1-5.

device 1 in comparison with devices 2 and 3. Notably, compared to device 5 using DCJTb, device 3 using emitter 3 showed the almost twice increased luminous and power efficiencies. Presumably, the bulky adamantane groups prevent the self-aggregation and thus suppress the formation of excimers of the emitting materials. This would lead the improved EL performances of device 3. In devices 3 and 4 using 3 as a dopant at the different doping concentrations, with the increase of doping concentration from 1% to 3%, the luminous and power efficiencies decreased due to the concentration quenching effect.

Although an efficient orange-red OLED using the emitter 3 has insufficient color purity for applications to full-color displays, Emitter 3 can be used to fabricate efficient white organic light-emitting diodes (WOLEDs). Recently, highly efficient WOLEDs by a combination of fluorescent sky-blue and red emitters with complementary colors has been demonstrated.¹² Therefore, emitter 3 is an excellent fluorescent red material for efficient WOLEDs with a combination of suitable sky blue emitters.^{13,14}

In conclusion, we designed and synthesized three julolidine- π -julolidine type emitting materials (1-3) with the bulky adamantane groups. To study their electroluminescent properties, the multilayered OLED devices with the structure of ITO/NPB (40 nm)/ADN : 1-3 (x%) (20 nm)/Alq₃ (40 nm)/

Liq (2 nm)/Al were fabricated. All devices using emitters 1-3 showed the efficient emissions, in which their EL performances depend on the structure of emitters sensitively. Particularly, a device using emitter 3 exhibited the efficient orange-red emission with the luminous and power efficiencies of 4.79 cd/A and 1.76 lm/W at 20 mA/cm², respectively. The CIE coordinates of this device was (0.57, 0.42) at 7.0 V.

Experimental Section

Materials and Measurement. ¹H-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 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.

General Procedure for Synthesis of 1-3. To a mixture of 5-(1,1-adamantyl-7,7-dimethyljulolidyl)carbaldehyde (2.2 eq.) and the corresponding bis-phosphonates (1.0 eq.) in anhydrous THF at 0 °C was added a solution of 1.0 M KO(*t*-Bu) (2.4 eq.) in THF under an Ar atmosphere. The reaction mixture was stirred for 10 min at 0 °C and then 1 h at room temperature. After the reaction had finished, the reaction mixture was quenched by water and then extracted with ethyl acetate. The organic layer was dried with anhydrous MgSO₄ and filtered. The mixture was evaporated and the residue purified by re-crystallization from dichloromethane and hexane.

1. Yield: 37.0%. ¹H-NMR (300 MHz, CDCl₃) δ 7.58 (d, 4H, *J* = 8.7 Hz), 7.52 (d, 4H, *J* = 8.4 Hz), 7.46 (s, 2H), 7.25 (s, 2H), 7.07 (d, 2H, *J* = 15.9 Hz), 6.86 (d, 2H, *J* = 16.2 Hz), 3.22-3.18 (m, 8H), 2.29-2.22 (m, 16H), 2.03-1.88 (m, 8H), 1.78-1.69 (m, 16H), 1.32 (s, 12H). ¹³C-NMR (75 MHz, CDCl₃) δ 136.5, 135.8, 134.2, 131.2, 129.1, 127.5, 126.4, 124.7, 122.5, 121.1, 117.2, 115.2, 113.3, 46.2, 45.8, 41.3, 39.7, 36.5, 35.1, 33.7, 32.1, 31.9, 31.2, 30.5, 28.3, 28.0. FAB-MS (*m/z*): 844 [M⁺]; HRMS: [EI⁺] calcd for C₆₂H₇₂N₂: 844.5696 [M⁺]. Found: 844.5691. mp 285 °C.

2. Yield: 30.0%. ¹H-NMR (300 MHz, CDCl₃) δ 8.71 (s, 2H), 8.33 (d, 2H, *J* = 7.5 Hz), 7.92 (d, 2H, *J* = 7.5 Hz), 7.47 (s, 2H), 7.26 (s, 2H), 7.15 (d, 2H, *J* = 16.0 Hz), 6.82 (d, 2H, *J* = 16.0 Hz), 3.23-3.18 (m, 8H), 2.29-2.20 (m, 12H), 2.02-1.90 (m, 8H), 1.78-1.71 (m, 16H), 1.32 (s, 12H). ¹³C-NMR (75 MHz, CDCl₃) δ 138.5, 137.1, 135.2, 134.1, 131.1, 129.5, 127.7, 126.5, 124.6, 122.2, 120.9, 116.8, 115.1, 112.8, 46.1, 45.7, 41.5, 39.6, 36.2, 35.6, 33.5, 32.7, 31.6, 31.0, 30.2, 28.2, 28.1. FAB-MS (*m/z*): 846 [M⁺]; HRMS: [EI⁺] calcd for

C₆₀H₇₀N₄: 846.5600 [M⁺]. Found: 846.5592. mp 267 °C.

3. Yield: 37.0%. ¹H-NMR (300 MHz, CDCl₃) δ 8.475 (m, 4H), 7.618 (d, 4H, *J* = 19.8 Hz), 7.403 (m, 6H), 6.763 (m, 2H), 3.238 (s, 8H), 2.269 (d, 12H, *J* = 12.0 Hz), 2.053 (m, 4H), 1.912 (d, 4H, *J* = 12.6 Hz), 1.766 (m, 16H), 1.302 (s, 12H); Mass (ESI) *m/z* 869.50 ([M+1]⁺); HRMS (EI⁺) calcd for C₆₄H₇₂N₂, 868.5696; found 868.5691. mp 291 °C.

Device Fabrication and Characterization. OLEDs were fabricated by vacuum (10⁻⁶ torr) thermal evaporation onto pre-cleaned ITO coated glass substrates. The device structures were as follows: ITO/*N,N'*-diphenyl-*N,N'*-(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) (50 nm)/9,10-di-(2-naphthyl)anthracene (ADN) : 1-3 (1 or 3%) (30 nm)/Alq₃ (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. Electroluminescence was measured using a Roper Scientific Pro 300i.

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