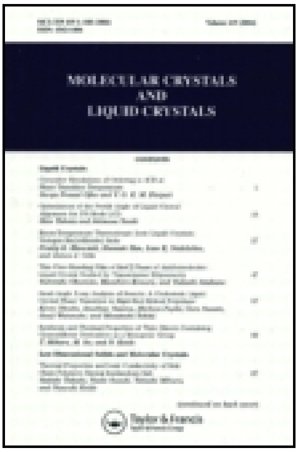

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of Donor-Aromatic-Donor Type π-conjugated Materials and their Application to Red Fluorescent Organic Light-Emitting Diodes

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Version of record first published: 02 Aug 2012.

To cite this article: Eun Jae Na , Kum Hee Lee , Young Kwan Kim & Seung Soo Yoon (2012): Synthesis of Donor-Aromatic-Donor Type π-conjugated Materials and their Application to Red Fluorescent Organic Light-Emitting Diodes, Molecular Crystals and Liquid Crystals, 563:1, 166-172

To link to this article: http://dx.doi.org/10.1080/15421406.2012.689155

Mol. Cryst. Liq. Cryst., Vol. 563: pp. 166–172, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.689155

Synthesis of Donor-Aromatic-Donor Type π-conjugated Materials and their Application to Red Fluorescent Organic Light-Emitting Diodes

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*A series of donor-aromatic-donor type π-conjugated materials were designed and synthesized. A device with the structure of ITO/NPB (50 nm)/Alq$_3$: **3** (1%) (30 nm)/Alq$_3$ (40 nm)/Liq (2 nm)/Al showed the luminous and power efficiencies of 3.57 cd/A and 1.65 lm/W at 20 mA/cm^2, respectively. The CIE coordinates of this device was (0.57, 0.41) at 7.0 V. This study demonstrates that the donor-aromatic-donor type π-conjugated materials are the promising materials for applications in white OLEDs.*

Keywords π-conjugated materials; donor-aromatic-donor; OLED; red fluorescent materials

Introduction

For the application of organic light-emitting diodes (OLEDs) in full-color flat panel display, 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 [3–9]. Recently, a variety of red fluorescent materials including the pyran containing materials [10–14], the arylamino-polyaromatic hydrocarbon derivatives [15], polyacenes [16], and metal chelates [17] have been widely studied. Particularly, Zhang group reported a new red fluorescent material based on N,N-bis{4-[2-(4-dicyanomethylene-6-methyl-4H-pyran-2-yl)ethylene]phenyl}aniline (BDCM) with two (4-dicyanomethylene)-4H-pyran electron-acceptor moieties and a triphenylamine electron-donor moiety, and showed the red electroluminescence with the power efficiency of 0.059 lm/W and the CIE coordinate of (0.63, 0.36) in an OLED device using this materials as a dopant [18]. Nevertheless, red materials EL performances still need to be improved for the high efficient practical applications.

In this paper, we describe the synthesis of a series of donor-aromatic-donor type π-conjugated materials (**1–3**) and their application to red fluorescent OLEDs. In materials **1–3**, two donor moieties, (3,3-adamantyl-7,7-dimethyl)julolidine, were connected through

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four different aromatic groups such as benzene, 2,5-dimethoxybenzene and pyrazine, 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 adamatane groups are introduced to prevent concentration quenching due to self-aggregation.

Experimental

Materials and Measurement

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.

General Procedure for synthesis of materials 1–3. To a mixture of 5-(3-adamantyl-7,7-dimethyljulolidyl)carbaldehyde (2.2 mmol) and the corresponding bis-phosphonates (1.0 mmol) in anhydrous THF at 0°C was added dropwise 1.0 M KO(*t*-Bu) (2.4 mmol) in THF under an Ar atmosphere. The reaction mixture was stirred for 10 min at 0°C followed by 1 h at room temperature. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The mixture was evaporated and the residue purified by re-crystallization from dichloromethane and hexane.

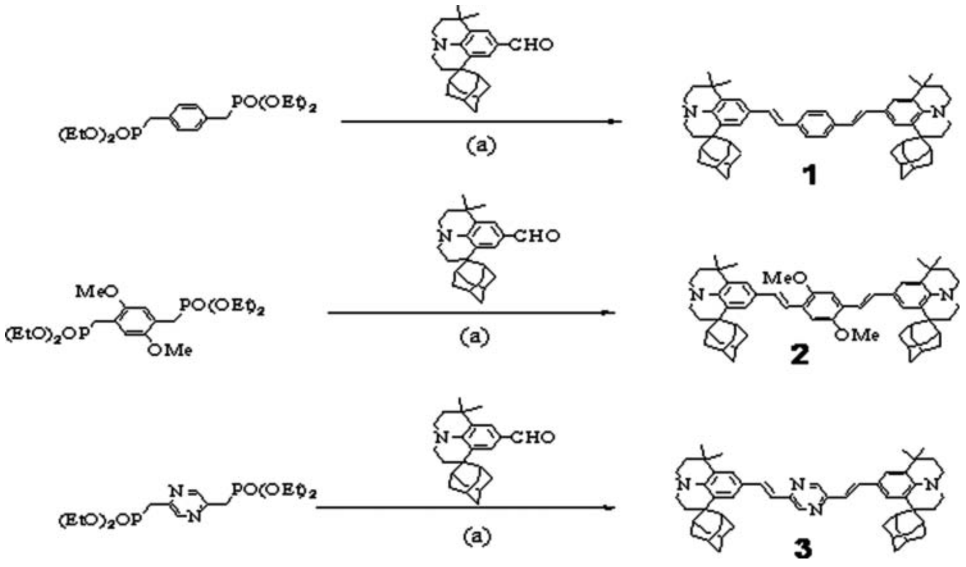
Synthesis of 1. Yield: 51.6%. ^{1}H-NMR (300 MHz, $CDCl_3$) [δ ppm]: 7.49 (m, 8H), 7.06 (d, $J = 15.6$ Hz, 2H), 6.88 (d, $J = 15.6$ Hz, 2H), 3.24 (s, 8H), 2.27-2.23 (m, 10H), 2.05-1.88 (m, 10H), 1.75-1.72 (m, 16H), 1.33 (s, 12H). FAB-MS (m/z): 768 [M+]; HRMS: [EI+] calcd for $C_{56}H_{68}N_2$: 768.5386, [M+]. Found: 768.5383.

Synthesis of 2. Yield: 54.3%. ^{1}H-NMR (300 MHz, $CDCl_3$) [δ ppm]: 7.45 (m, 4H), 7.01 (d, $J = 15.8$ Hz, 2H), 6.82 (m, 4H), 3.72 (s, 6H), 3.22 (s, 8H), 2.27-2.23 (m, 10H), 2.05-1.88 (m, 10H), 1.75-1.72 (m, 16H), 1.33 (s, 12H). FAB-MS (m/z): 829 [M+]; HRMS: [EI+] calcd for $C_{58}H_{72}N_2O_2$: 828.5594, [M+]. Found: 828.5590.

Synthesis of 3. Yield: 58.6%. ^{1}H-NMR (300 MHz, $CDCl_3$) [δ ppm]: 7.67 (s, 2H), 7.41 (m, 4H), 7.11 (d, $J = 16.2$ Hz, 2H), 6.95 (d, $J = 16.1$ Hz, 2H), 3.25 (s, 8H), 2.27-2.23 (m, 10H), 2.05-1.88 (m, 10H), 1.75-1.72 (m, 16H), 1.33 (s, 12H). FAB-MS (m/z): 771 [M+]; HRMS: [EI+] calcd for $C_{54}H_{66}N_4$: 770.5287, [M+]. Found: 770.5282.

Fabrication of PLED

OLEDs using 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 by N_2 gas. The device structures were as follows: (1) ITO/*N*,*N′*-diphenyl-*N*,*N′*-(1-napthyl)-(1,1′-biphenyl)-4,4′-diamine (NPB) (40 nm)/tris(8-quionlinolato)-aluminium (Alq_3) : Red dopant (x%) (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 1′Éclairage (CIE) coordinate characteristics were measured using a Keithly 2400 source measurement



Scheme 1. Synthesis and structures of materials **1–3**. (a) KtOBu.

unit and a Chroma meter MINOLTA CS-1000A. Electro-luminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

Structures and synthetic scheme of materials **1–3** were shown in Scheme 1. Synthesis of **1–3** began with the preparation of 5-(3,3-adamantyl-7,7-dimethyl)julolidine carboaldehyde by following the known procedure [19]. Subsequently, Honor-Emmons reaction with the corresponding bis-phosphonates provided materials **1–3** with the moderate yield. These materials were fully characterized with ^{1}H-NMR, low- and high-resolution mass spectrometry.

The ultraviolet-visible (UV-Vis) absorption and emission spectra of materials **1–3** are shown in Fig. 1(a) and (b). The maximum absorption peaks of these materials were 432, 445

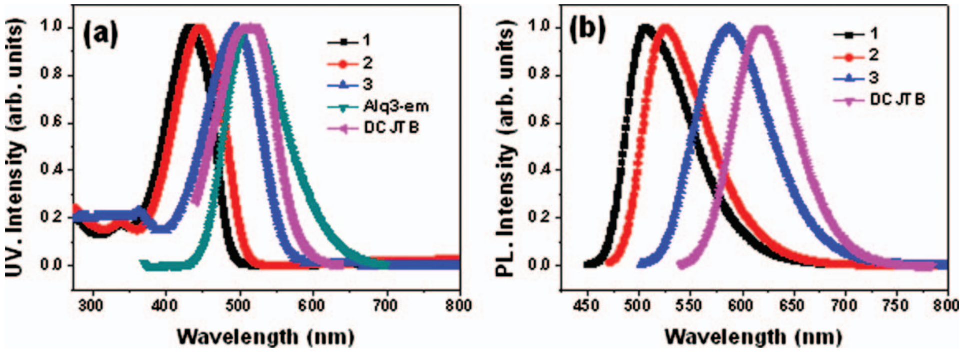


Figure 1. (a) UV-Vis spectra and (b) PL spectra of materials **1–3**.

Table 1. Photophysical properties of materials **1**–**3**

Compound	$\lambda_{max}{}^a$ [nm]	$\lambda_{max}{}^b$ [nm]	FWHM [nm]	HOMO/LUMO [eV]	E_g	Φ^c
1	432	505	73	−5.37/−2.77	2.60	0.38
2	445	526	71	−5.36/−2.85	2.51	0.57
3	494	588	84	−5.35/−2.97	2.42	0.46
DCJTB	511	619	72	−5.26/−3.10	2.16	0.78

[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** ($\Phi = 0.78$) [20].

and 494 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 material **3**. This observation imply that the Förster singlet energy transfer from host Alq_3 to material **3** would be efficient, and Alq_3 served well as a host in the OLEDs by using **3** as red dopant material. Materials **1**–**3** exhibit efficient emissions with maximum emission peaks of 505, 526 and 588 nm, respectively, as shown in Fig. 1(b). Material **3** showed the efficient orange-red emission, while materials **1** and **2** showed the green emissions. Presumably, the charge-transfer band in donor-acceptor-donor type material **3** would lead the red-shifted emission of **3** in comparison with materials **1** and **2**. All physical properties were shown in Table 1. Material **3** was selected for electroluminescent measurement because of suitable emission wavelength for red fluorescent OLEDs. Multilayer devices were fabricated as follows: ITO/NPB (50 nm)/Alq_3: **3** (1 and 3%) (30 nm)/Alq_3 (40 nm)/Liq (2 nm)/Al. NPB, Alq_3, and Liq were used for hole transporting layer, red host and electron transporting layer, and electron injection layer, respectively. The performance characteristics of these devices are summarized in Table 2.

The luminous and power efficiencies of devices are shown in Fig. 2. Also, the EL spectra of devices are shown in Fig. 3. The maximum luminous efficiency of devices **1** and **3** using **3** and **DCJTB** as dopants at the same doping concentration were 3.61 and 2.52 cd/A, respectively. The luminous efficiency of devices **1** and **3** were 3.57 and 2.38 cd/A at 20 mA/cm^2, respectively. And the maximum power efficiency of devices **1** and **3** were 1.72 and 1.32 lm/W, respectively. Notably, compared to device **3** using **DCJTB**, the maximum luminous and power efficiency of device **1** using **3** increased by 43 and 30%, respectively. The bulky adamantly group of dopant **3** of device **1** could prevent molecular aggregation and thus reduce concentration quenching. This would contribute to the improved luminous

Table 2. EL performance characteristic of devices **1**–**3**

Device	Dopant (%)^a	L^b (cd/m^2)	LE$^{c/d}$ (cd/A)	PE$^{c/d}$ (lm/W)	EL (λ_{max}) (nm)	FWHM (nm)	CIE^e (x,y)
1	3 (1.0)	10480	3.61/3.57	1.72/1.65	606	68	(0.57, 0.41)
2	3 (3.0)	5245	1.99/1.98	0.95/0.89	609	78	(0.58, 0.40)
3	**DCJTB** (1.0)	6300	2.52/2.38	1.32/1.08	616	104	(0.60, 0.39)

[a]Doping concentration. [b]Maximum luminance. [c]Maximum value. [d]At 20 mA/cm^2. [e]Commission Internationale d′Énclairage (CIE) coordinates at a 7.0 V.

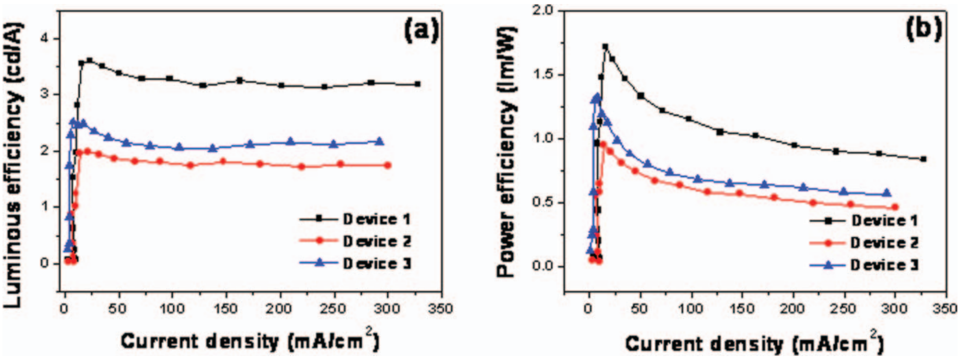


Figure 2. (a) Luminous efficiencies-current density and (b) power efficiencies-current density characteristics of devices **1**–**3**.

efficiency of device **1** [21]. In devices **1** and **2** 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.

The EL spectra of devices **1** and **2** using dopant **3** showed the maximum emission peaks of 606 and 609 nm, respectively. The CIE coordinates of devices **1** and **2** are (0.57, 0.41) and (0.58, 0.40), respectively, in the orange-red region of visible spectrum. Although an efficient orange-red OLED using **3** has insufficient color purity for applications to full-color displays, material **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 orange-red emitters with complementary colors has been demonstrated [22]. Therefore, **3** is an excellent fluorescent orange-red material for efficient WOLEDs with a combination of suitable sky blue emitters [23–26].

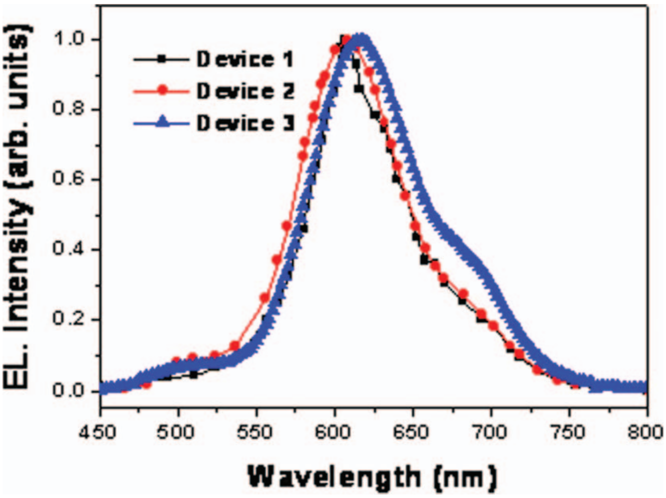


Figure 3. EL spectra the devices **1**–**3**.

Conclusions

We designed and synthesized a series of donor-aromatic-donor type π-conjugated materials. A device with the structure of ITO/NPB (50 nm)/Alq$_3$: **3** (1%) (30 nm)/Alq$_3$ (40 nm)/Liq (2 nm)/Al showed the luminous and power efficiencies of 3.57 cd/A and 1.65 lm/W at 20 mA/cm^2, respectively. The CIE coordinate of this device was (0.57, 0.41) at 7.0 V. Compared to a device using **DCJTB**, this device showed the improved EL performances due to reduced the molecular aggregation resulting in prevented concentration quenching. This study demonstrates that the donor-aromatic-donor type π-conjugated materials are the promising materials for applications in white OLEDs.

Acknowledgment

This research was supported by Basic Science Research Program through the NRF funded by the Ministry of Education, Science and Technology (20110004655).

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