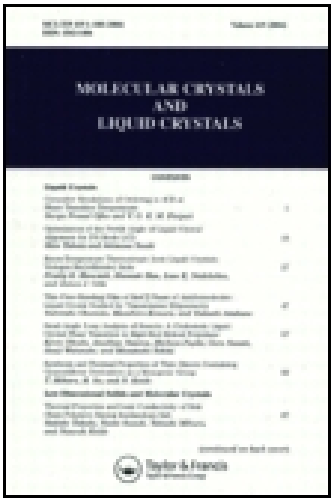

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Electroluminescent Properties of Novel Fluorene Derivatives with Aromatic Amine Moieties

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2,7-Bis[(4-diphenylamino)phenylvinylene]-9,9-diethylfluorene(BDPDF, **1***) and 2,7-bis[(9-ethyl-3-carbazolylvinylene)-9,9-diethylfluorene(BECDF,* **2***) have been synthesized and characterized. To evaluate electroluminescent performance, compound* **1** *and* **2** *were used as emitting materials and dopant materials, respectively and the basic device structure was ITO/m-MTDATA/α-NPD/***1** *or* **2** *or doped DPVBi with* **1** *or* **2***/Alq_3/LiF/Al.*

*The devices using BDPDF(***1***) and BECDF(***2***) show EL peak at 470 nm and 486 nm. The device showed a blue light-emission with the CIE chromaticity coordinates of (0.177, 0.268).*

Keywords: aromatic amine; doping agent; electroluminescence; fluorene

1. INTRODUCTION

Since the electroluminescent devices based on small organic molecules [1] were first developed, the search for new electroluminescent materials

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and the study on the optimization of device structure have expanded rapidly. In this regard, there has been a considerable interest in developing efficient and stable organic blue light-emitting device to achieve full-color display application. Many blue electroluminescent materials have been synthesized [2–5]. The blue doped emitter in OLED often necessitates the judicious selection or design of an appropriate blue host material which has a wide enough band gap energy and a set of matching LUMO/HOMO level to effect the sensitization. In commercial circles, one of the best blue emitters used in OLED is believed to have been patented by Idemitsu Kosan Co. based on the basic structure of distyrylarylene (DSA) host doped with a hole transporting amine-substituted DSA Dopant [6]. This doped blue emitter could achieve a luminous efficiency of $>6\,\mathrm{lm/W}$ at $100\,\mathrm{cd/m^2}$ with a lifetime of continuous DC operation of $>30{,}000\,\mathrm{h}$, but blue emitters and dopants still remain the most sought-after material.

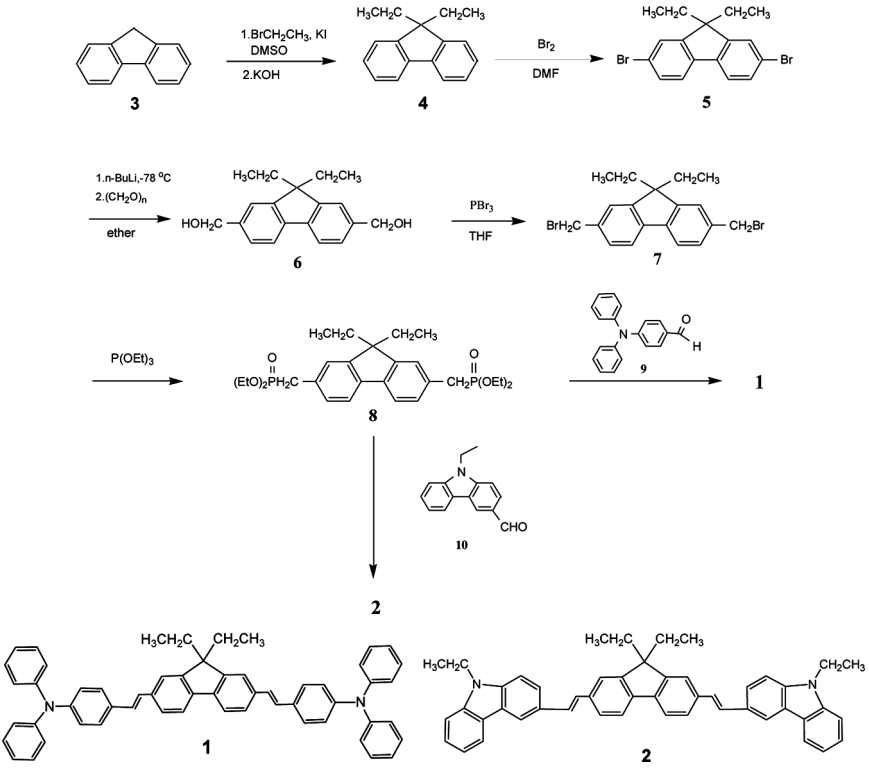
In this paper, we report the synthesis and characterization of new fluorene derivatives with triphenylaminovinylene and carbazolylvinylene moieties, i.e., 2,7-bis[(4-diphenylamino)phenylvinylene]-9,9-diethylfluorene(BDPDF, **1**) and 2,7-bis(9-ethyl-3-carbazolylvinylene) -9,9-diethylfluorene(BECDF, **2**). These two compounds are used as emitting materials, and then as dopant materials to the host compound, DPVBi in the basic device structure; ITO/m-MTDATA/ α-NPD/**1** or **2**/Alq_3/LiF/Al.

2. EXPERIMENTS

BDPDF(**1**) and BECDF(**2**) were synthesized by Witting-Horner reaction of the precursor phosphonate **8** with aldehydes **9** and **10**, respectively, as described in Scheme 1.

2.1. 2,7-Bis[(4-diphenylamino)phenylvinylene]-9,9-diethylfluorene(BDPDF, 1)

A solution of 2,7-bis(methyldiethoxyphosphonate)-9,9-diethylfluorene (1.33 g, 2.50 mmol) and 4-diphenylaminobenzaldehyde (2.40 g, 8.80 mmol) in THF (30 ml) was stirred at room temperature for 3 h, and then NaH (0.30 g, 12.5 mmol) was added. The reaction mixture was stirred for 20 h, diluted with water and then extracted with CH_2Cl_2. After evaporation of solvent in vacuum, the crude product was chromatographed on silica gel with CH_2Cl_2/hexane (1:2) and then recrystallized from MeOH/$CHCl_3$ (1:75) to give a pure solid product (0.97 g, 51%).



SCHEME 1 Synthesis of BDPDF(**1**) and BECDF(**2**).

^{1}H-NMR($CDCl_3$, 400 MHz): $\delta = 7.40 - 7.00$ (m, 38H, Ar-H), 2.07 (q, 4H, CH_2), 0.37 (t, 6H, CH_3). FT-IR(KBr): 2962, 2917, 1591, 1508, 1492, 1280 cm^{-1}.

2.2. 2,7-Bis(9-ethyl-3-carbazolylvinylene)-9,9-diethylfluorene(BECDF, 2)

BECDF was synthesized with same procedure as BDPDF's (Final step yield: 51%).

^{1}H-NMR($CDCl_3$, 400 MHz): $\delta = 8.30 - 7.10$ (m, 24H, Ar-H), 4.40 (q, 4H, CH_2), 2.10 (q, 4H, CH_3), 0.35 (t, 6H, CH_3). FT-IR(KBr): 3020, 2962, 1596 cm^{-1}.

3. RESULT AND DISCUSSION

Figures 1 and 2 show the UV-absorption and photoluminescence (PL) spectra of the two emission layers in thin films on quartz plates. The

maximum absorption of BDPDF(1) appeared at 410 nm, and the absorption edge of BDPDF(**1**) at 475 nm. For BECDF(2), the maximum absorption appeared at 404 nm and the absorption edges at 460 nm.

The energy band gap of BDPDF and BECDF was 2.67 eV and 2.74 eV according to UV absorption edge calculation. The HOMO energy level of these materials was calculated from the onset potential of cyclic voltammogram by assuming the absolute energy level of ferrocene(FOC) is 4.80 eV [7] and it gave 5.90 eV (BDPDF) and 6.00 eV (BECDF), respectively.

We measured I-V characteristics and luminance-current-voltage characteristics of related EL devices. The device structure was ITO 150 nm/m-MTDATA 42 nm/α-NPD 12 nm/BDPDF or BECDF or doped DPVBi 24 nm/$Alq_3$24 nm/LiF 1 nm/Al 200 nm and doped DPVBi was doped with BDPDF or BECDF.

Figure 3 shows forward-biased current-voltage (I-V) intensity curves for the undoped organic EL device. These curves were obtained when the devices were operated in a continuous direct current (dc) mode under forward bias (positive voltage applied to the ITO contact). These device exhibit diode characteristics, that is, forward current increases with increasing forward bias voltage. The turn-on voltage of these devices is about 4.50 V at a current density of approximately

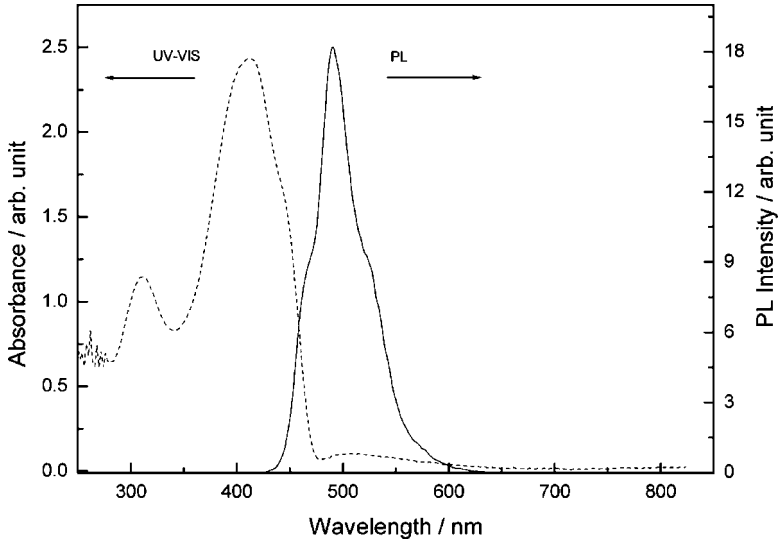


FIGURE 1 UV-visible (dot line) and photoluminescence (solid line) spectra of BDPDF thin film on quartz substrate (excitation wavelength 410 nm).

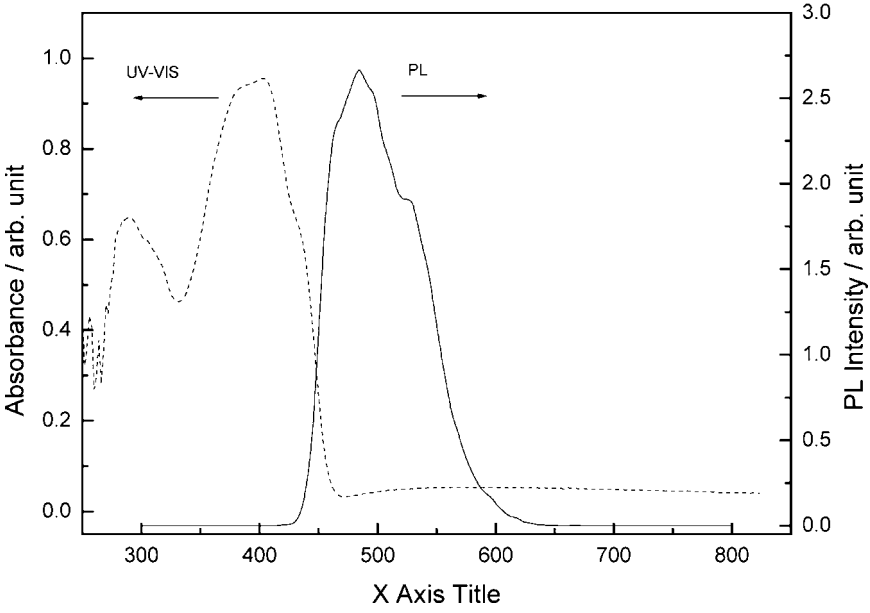


FIGURE 2 UV-visible (dot line) and photoluminescence (solid line) spectra of BECDF thin film on quartz substrate (excitation wavelength 404 nm).

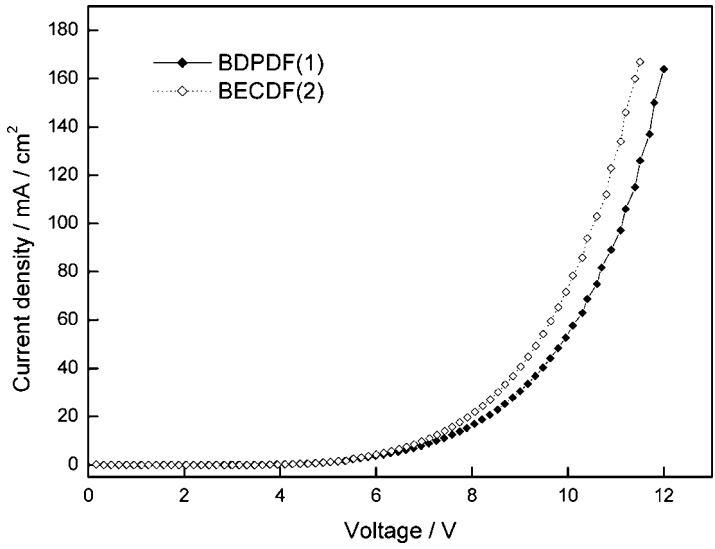


FIGURE 3 Current-voltage (I-V) characteristics of undoped EL devices.

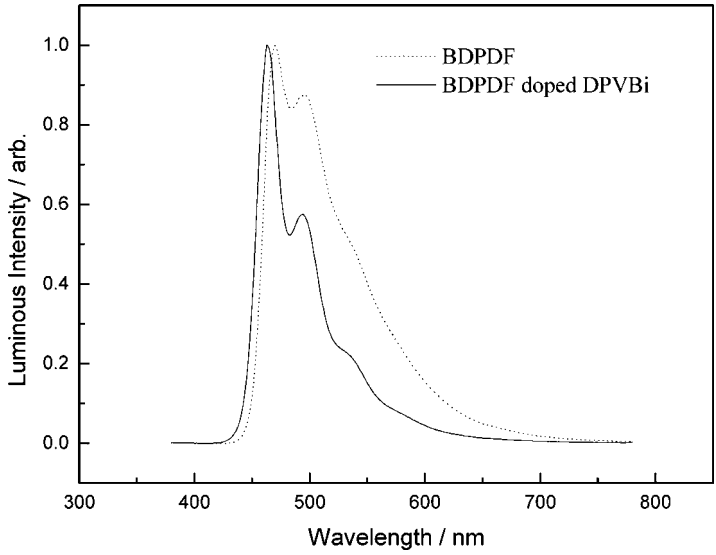


FIGURE 4 EL spectra of devices using BDPDF as an emissive layer (dot line) and doped into DPVBi (solid line).

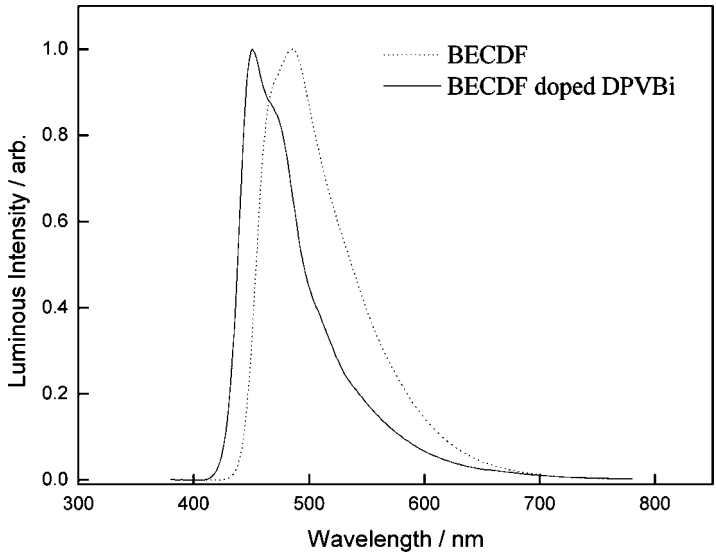


FIGURE 5 EL spectra of devices using BECDF as an emissive layer (dot line) and doped into DPVBi (solid line).

TABLE 1 Luminescent Properties of the Devices Using BDPDF(**1**) and BECDF(**2**) as an Emitting Layer

Emitting material	EL peak [nm]	Efficiency [l m/W] @ 120 cd/m^2	Efficiency [cd/A]	Voltage [V] @ 120 cd/m^2	CIE coordinate	
					x	y
(**1**)	470	0.15	0.45	9.6	0.238	0.404
(**1**)-doped DPVBi	464	0.83	1.91	7.2	0.177	0.268
(**2**)	486	0.56	1.30	7.3	0.222	0.380
(**2**)-doped DPVBi	451	0.24	0.68	8.6	0.183	0.213

500 μA/ cm^2, depending upon the total thickness of the organic EL devices.

Figures 4 and 5 show the EL spectra of the devices using BDPDF, BECDF as emitting layers, together with those of the devices using BDPDF, BECDF as a guest material to DPVBi, respectively. In Figure 4, the EL spectrum of the device using BDPDF as an emitting layer peaks at 470 nm. As a result, the device shows a greenish blue emission with the CIE chromaticity coordinates of (0.238, 0.404) and luminous efficiency of 0.45 cd/A. When the BDPDF doped into DPVBi, the EL peak of the device is shifted to shorter wavelength, which is at 464 nm, and the device emits a sky blue light with the CIE chromaticity coordinates of (0.177, 0.268). The maximum luminous efficiency of doped device with BDPDF shows 1.91 cd/A (as shown in Table 1).

In Figure 5, the EL peak of BECDF shows at 486 nm, which is almost same wavelength as compared to the PL spectrum, as illustrating in Figure 2. The device also shows a greenish blue emission with the CIE chromaticity coordinates of (0.222, 0.380) and luminous efficiency of 1.3 cd/A. However, the BECDF-doped device using DPVBi as a host material shows lower luminous efficiency compared to doped device with BDPDF, which is 0.68 cd/A. The EL characteristics of these blue-emitting devices are summarized in Table 1.

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