

# A High Performance Nondoped Blue Organic Light-Emitting Device Based on a Diphenylfluoranthene-Substituted Fluorene Derivative

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A new blue light-emitting fluorene derivative 2,7-di[8-(7,10-diphenylfluoranthenyl)]-9,9-dimethylfluorene (DFDF) with good thermal stability at 420 °C has been synthesized and characterized. An organic light-emitting device (OLED) with the structure of ITO/NPB (70 nm)/DFDF (30 nm)/TPBI (20 nm)/LiF (0.5 nm)/Al (100 nm) has been investigated, where DFDF serves as a nondoped host emitter. Such a device possesses high current and power efficiencies of 3.8 cd/A and 2.6 lm/W, respectively, and stable bright blue-light emission at  $\lambda = 474$  nm with Commission Internationale de L'Eclairage coordinates of (0.16, 0.23) over a wide range of operating voltages. The present results verify that DFDF is a promising candidate for a fluorescent blue-light-emitting OLED.

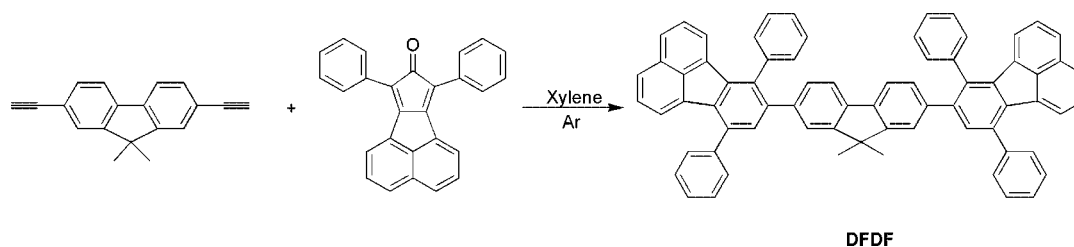
## 1. Introduction

Since the pioneering work of multilayered organic light-emitting devices (OLEDs),<sup>1</sup> this research field has attracted extensive attention because of its huge market potential in the next-generation flat-panel display technology.<sup>2</sup> During the past two decades, many high-performance materials with desirable properties have been developed to meet the requirements of full-color displays.<sup>1–4</sup> Blue light-emitting material not only can generate white light in combination with complementary yellow light emission but also can function as a host for dopant emitters because of its intrinsic large energy bandgap. However, in

contrast to green light-emitting materials, further improvement is needed in the performance of blue light-emitting materials in terms of device efficiencies and color purity. Particularly, it is important to develop high-performance blue light-emitting materials with good thermal and morphological stability as well as high fluorescence efficiency.

In this paper, we report the synthesis and characterization of a novel fluorene derivative, namely 2,7-di[8-(7,10-diphenylfluoranthenyl)]-9,9-dimethylfluorene (DFDF). The 7,10-diphenylfluoranthene substituent is introduced because of its emissive and rigid properties, which are expected to improve the fluorescence quantum yield and thermal stability of the fluorene derivative. A nondoped device based on the fluorene derivative DFDF has been prepared and shown to have a stable blue light emission

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**SCHEME 1: Synthetic Route to DFDF**

at a wavelength of 474 nm with the Commission Internationale de L'Éclairage (CIE) coordinates of (0.16, 0.23). In addition, the device exhibits a high current and power efficiencies of 3.8 cd/A and 2.6 lm/W, respectively, which are comparably high as those of any nondoped fluorescence blue-light-emitting OLEDs ever reported.

**2. Experimental Section**

**2.1. Material Synthesis.** The fluorene derivative DFDF was synthesized according to the Diels–Alder reaction (Scheme 1). 2,7-Diethynyl-9,9-dimethylfluorene<sup>5</sup> and 7,9-diphenyl-8*H*-cyclopenta[1]acenaphthylene-8-one<sup>6</sup> were synthesized according to the literature procedures. All solvents were purified by routine procedures. Other reagents in the scheme were used as received from commercial sources.

**2.2. Synthesis of DFDF.** 2,7-Diethynyl-9,9-dimethylfluorene (363 mg, 1.5 mmol) and 7,9-diphenyl-8*H*-cyclopenta[1]acenaphthylene-8-one (1.17 g, 3.3 mmol) were dissolved in *o*-xylene (20 mL) under argon atmosphere, and the resultant mixture was heated for 24 h at 170 °C (oil bath temperature). After the mixture was cooled to room temperature, ethanol (100 mL) was added. The precipitate was filtered, washed with ethanol (200 mL), and dried in a vacuum. Following column chromatography (petroleum ether:CH<sub>2</sub>Cl<sub>2</sub>, 5:1) on silica gel, DFDF was obtained as a slightly yellow and strongly fluorescent solid. Yield: 88%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 7.79–7.71 (m, 8H), 7.58–7.53 (m, 8H), 7.42–7.36 (m, 14H), 7.36–7.28 (m, 6H), 7.14 (d, *J* = 1.5, 2H), 6.74 (d, *J* = 7.2, 2H), 1.53 (s, 6H). MS (*m/z*): 899 (*M* + 1). Anal. Calcd for C<sub>71</sub>H<sub>46</sub>: C, 94.84; H, 5.16. Found: C, 94.81; H, 5.23.

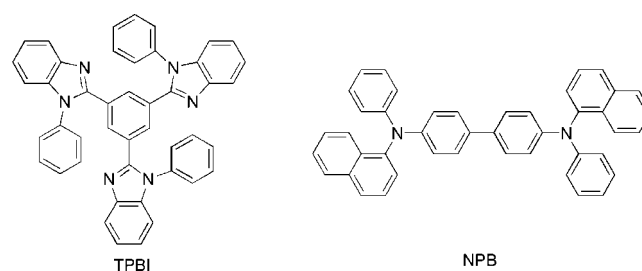
**2.3. Device Fabrication and Characterization.** Patterned indium tin oxide (ITO) glass substrates with a sheet resistance of 30 Ω per square were cleaned with isopropyl alcohol, Decon 90, rinsed in deionized water, dried in an oven, and finally treated in an ultraviolet–ozone chamber. The ITO substrates were then transferred into a deposition chamber with a base pressure of 10<sup>−6</sup> mbar. The device with a configuration of ITO/NPB (70 nm)/DFDF (30 nm)/TPBI (20 nm)/LiF (0.5 nm)/Al (100 nm) was prepared by thermal vapor deposition [NPB and TPBI are *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene, respectively]. Figure 1 depicts the chemical structures of NPB and TPBI. Deposition rates were monitored with a quartz oscillation crystal and controlled at 0.1–0.2 nm/s for both organic and metal layers. A shadow mask was used to define the cathode to make four 0.1 cm<sup>2</sup> devices on each substrate. Electroluminescence (EL) spectra and current density–voltage–luminance (J–V–L) characteristics of OLEDs were measured with a programmable Keithley model 237 power source and a Spectrascan PR 650 photometer under ambient air conditions. Absorption and photoluminescence (PL) spectra of DFDF were measured with a Perkin-Elmer Lambda UV-vis spectrometer. The ionization potential (*I*<sub>p</sub>) of DFDF was measured with

ultraviolet photoelectron spectroscopy (UPS) in a VG ESCALAB 220i-XL surface analysis system, while the electron affinity (*E*<sub>A</sub>) was estimated by subtracting from *I*<sub>p</sub> the optical bandgap determined by the absorption spectrum of its solid-state film.

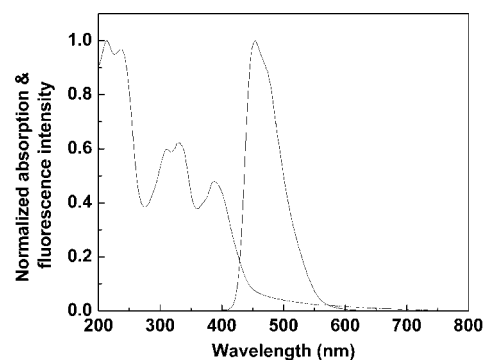
**3. Results and Discussion**

**3.1. Photophysical Properties of DFDF.** Figure 2 shows the absorption and PL spectra of thermally evaporated thin film of DFDF on a quartz substrate. DFDF shows the absorption peaks at 388, 330, 311, 236, and 213 nm and exhibits a strong PL emission peak at 455 nm upon direction excitation at 388 nm.

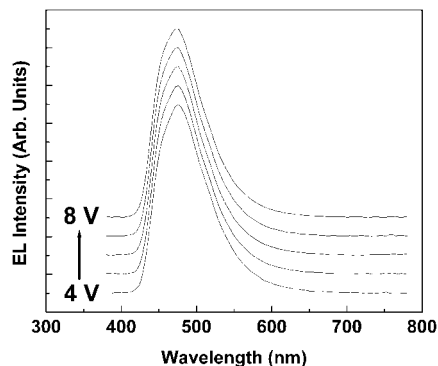
**3.2. Device Characteristics of DFDF.** To evaluate the EL performance, OLED with the architecture of ITO/NPB/DFDF/TPBI/LiF/Al was fabricated, where NPB, DFDF, and TPBI served as a hole-transporting material, a light emitter, and an electron-transporting material, respectively. DFDF was prepared in-house according to the synthesis route in Scheme 1, and its structure was confirmed with mass spectrometry, <sup>1</sup>H nuclear magnetic resonance, and elemental analyses. DFDF possesses a high decomposition temperature of 420 °C, which suggests good thermal stability. It is well-known that the EL features of OLEDs are generally dependent on the driving voltage because of the shift of emission zone. It is mainly attributed to the difference in charge carrier mobility in the organic layers under



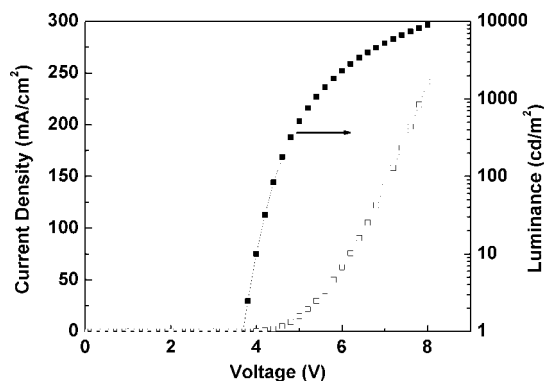
**Figure 1.** Chemical structures of NPB and TPBI.



**Figure 2.** Absorption and PL spectra of thermally evaporated thin film of DFDF on a quartz substrate.



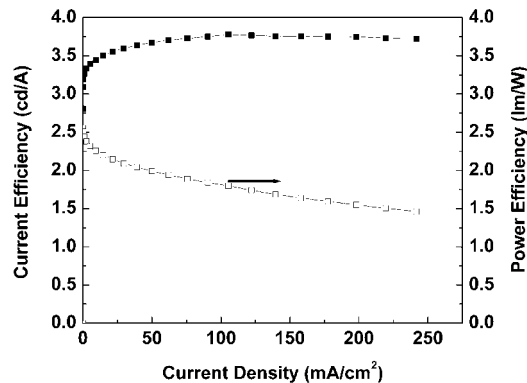
**Figure 3.** EL spectra of the DFDF-based device viewed in the normal direction at the driving voltages of 4–8 V.



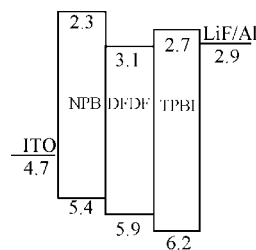
**Figure 4.** Current density–voltage–luminance characteristics of the DFDF-based device.

the same electric field. However, this phenomenon is not observed for the DFDF-based device. Figure 3 depicts the EL spectra of the DFDF-based device viewed in the normal direction at the driving voltages of 4–8 V. The present device using DFDF as a blue light emitter yields an EL emission peak at 474 nm with a full spectral width at half-maximum of about 76 nm. Significantly, the device exhibits a negligible change of CIE coordinates from (0.16, 0.24) to (0.16, 0.23) when the driving voltage increases from 4 to 8 V. The insensitivity of emission color to driving voltage suggests that the amount of electrons and holes are well balanced for recombination within the DFDF layer over a wide range of electric fields.

Figure 4 shows the plot of current density and luminance against driving voltage for the DFDF-based device. It can be seen that the driving voltage required to obtain a luminance of 100 cd/m<sup>2</sup> (the typical brightness for display applications) was as low as 4.4 V while the turn-on voltage (defined as the voltage needed to obtain a luminance of 1 cd/m<sup>2</sup>) was only 3.7 V. The current efficiency of the DFDF-based device remains almost constant over a wide range of current densities, as shown in Figure 5. For instance, the device attained a high current



**Figure 5.** Current efficiency–current density–power efficiency characteristics of the DFDF-based device.



**Figure 6.** Energy level diagram for the DFDF-based device.

efficiency of 3.5 cd/A at  $J = 14$  mA/cm<sup>2</sup> and remained unchanged even at  $J = 250$  mA/cm<sup>2</sup>. In addition, the device exhibited a maximum current and power efficiencies of 3.8 cd/A ( $\eta_{\text{ext}} = 2.3\%$ ) and 2.6 lm/W, respectively. These relatively high efficiencies are comparable to those previously reported for nondoped fluorescence blue-light-emitting OLEDs<sup>7–10</sup> and can be explained by the balance of electron and hole currents inside the emissive DFDF layer. The performance improvement relies on the effective electron and hole-blocking ability by using a low  $E_A$  of NPB (2.3 eV) and a high  $I_P$  of TPBI (6.2 eV), respectively, resulting in the confinement of opposite charges inside the light-emitting DFDF layer and thus high device efficiencies. As depicted in Figure 6, DFDF has a high  $E_A$  of 3.1 eV and a high  $I_P$  of 5.9 eV. It is expected that electrons and holes are confined at the NPB/DFDF interface, contributing to blue light emission. For comparison, the device performance of the current DFDF-based device is tabulated in Table 1 together with those of the recently reported blue OLEDs with nondoped and doped host light emitters. The DFDF-based device shows comparable performance to those of other blue OLEDs,<sup>7–10</sup> in terms of power efficiency and turn-on voltage, although its color purity still has room for improvement. It is worth noting that the distinct difference from other blue OLEDs is that no anode buffer layer of copper phthalocyanine (CuPc) has been used for the present device. It is expected that the device efficiency can be further increased by using the appropriate

**TABLE 1: Performance Parameters of the Present and Several Recently Reported Blue OLEDs<sup>a</sup>**

light-emitter	turn-on voltage [V]	maximum power efficiency [lm/W]	emission peak [nm]	CIE coordinates [x, y]	reference
DFDF <sup>b</sup>	3.7	2.6	474	0.16, 0.23	this work
PPP	3.7	3.0	474	0.14, 0.20	7
DPF	5.2	3.0	469	0.16, 0.22	8
TBP:Spiro-FPA	n.a.	2.1	465	0.13, 0.21	9
TBP:ADN	n.a.	1.8	465	0.15, 0.23	8, 10

<sup>a</sup> PPP, 1-(4-(1-pyrenyl)phenyl)pyrene; DPF, 2,7-dipyrene-9,9'-dimethylfluorene; TBP, 2,5,8,11-tetra-*tert*-butylperylene; spiro-FPA, 2,2'-bis(10-phenylanthracen-9-yl)-9,9'-spirobifluorene; ADN, 9,10-di(2-naphthyl)anthracene. <sup>b</sup> No anode buffer layer of copper phthalocyanine (CuPc) is used.

anode buffer layer. Nevertheless, the present results demonstrate that the fluorene derivative DFDF is a promising candidate for blue light-emitting OLEDs.

#### 4. Conclusions

In summary, the synthesis and characterization of a new fluorene derivative DFDF have been presented. The nondoped device based on DFDF as the light emissive layer shows a stable color purity of (0.16, 0.23) over a wide range of driving voltages, as well as a high current and power efficiencies of 3.8 cd/A ( $\eta_{\text{ext}} = 2.3\%$ ) and 2.6 lm/W, respectively. The performance improvement may be attributed to the balanced electron and hole currents within the light emissive DFDF layer.

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