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High-Efficiency Nondoped Deep-Blue-Emitting Organic Electroluminescent Device

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A new blue emitter, 9,9-bis-(3- (9-phenyl-carbazoyl))-2,7-dipyrenylfluorene (DCDPF), has been synthesized and characterized. Organic light-emitting devices (OLEDs) using DCDPF as a nondoped emitter exhibits deep-blue emission with a peak at 458 nm and CIE coordinates of (0.15, 0.15). The maximum efficiency of the device is 4.4 cd/A (3.1 lm/W). The results suggest that the introduction of carbazole units at the 9-position of fluorene provides an effective way to suppress molecular aggregation which would cause red shift in emission.

Introduction

Since the pioneering work on organic light-emitting devices (OLEDs) by the Kodak group, extensive research has been carried out to bring OLEDs into commercial applications in flat-panel displays and solid-state lightings.[1,2] To produce high-efficiency OLEDs, a key approach is to develop high-performance electroluminescent materials including RGB (red, green, blue) emitters. Many new materials including phosphorescent and fluorescent emitters of different colors have been developed to meet the demands of full-color displays. Phosphorescent OLEDs based on the organo-transition metal complexes, especially iridium (Ir) complexes, are of great interest because of the feasibility to achieve an internal quantum efficiency up to 100%.[3] Performances of green and red-emitting phosphorescent OLEDs are, in general, much higher than those of fluorescent OLEDs.[4−7] However, performance of blue phosphorescent emitter remains a bottleneck. Furthermore, other than the widely used FIrPic, there are few alternatives of blue phosphorescent emitters. However, FIrPic is in fact a blue-green emitter, with two peaks at 472 and 500 nm, respectively.[8,9] The color purity of the OLEDs based on FIrPic is thus compromised. Moreover, it is known that FIrPic-based devices are accompanied by fast degradation which means a short lifetime.[10] Till now, deep blue phosphorescent emitters with a long lifetimes have been scarce. Therefore, blue fluorescent emitters should still play a key role in the future applications of OLEDs.

The color purity and efficiency of most blue OLEDs are often mutually compromised. While many blue fluorescent emitters have been reported, materials emitting in the deep-blue region with high efficiency are still rare.[11−21] Thus, there is still much need for improvements in both efficiency and color purity of blue OLEDs, especially with an undoped device structure.

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In this paper, we report the synthesis and characterization of a new compound, 9, 9-bis-(3-(9-phenyl-carbazoyl))-2,7-dipyrenylfluorene (DCDPF). Although the carbazole/fluorene hybrids have been reported as host materials for phosphorescent OLEDs,[22] the reports about carbazole/fluorene/pyrene hybrids being used as deep-blue emitters are still absent. Our results suggest that introduction of the carbazole units at the 9-position of fluorene is an effective way to avoid molecular aggregation of the molecules and the associated red shift in emission. Moreover, the carbazole units also improve hole injection and transport properties. OLEDs based on DCDPF have been fabricated in a nondoped device structure, which exhibits deep-blue emission with a peak at 458 nm and CIE coordinates of (0.15, 0.15). The maximum efficiency of the blue OLED is 4.4 cd/A (3.1 lm/W), which is among the best values ever reported for nondoped deep blue fluorescence OLEDs.

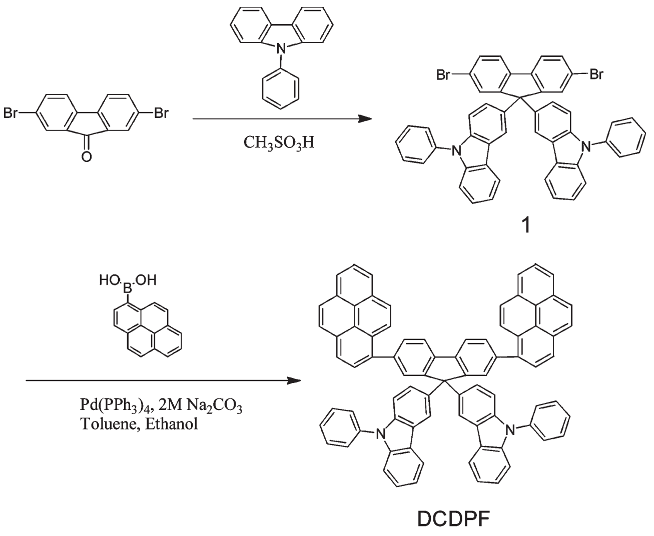
Experimental Details

Material Synthesis. *Compound **1**, 9,9-Bis-(3-(9-phenyl-carbazoyl))-2,7-dibromofluorene (**1**).* A mixture of 2,7-dibromofluorenone, (1.01 g, 3 mmol), 9-phenyl-carbazole (12.1 g, 50 mmol), and methane sulfonic acid (0.3 g, 3 mmol) was heated at 140 °C under a nitrogen atmosphere for 10 h. After being cooled, the mixture was extracted with dichloromethane (CH_2Cl_2). The organic solution was washed with sodium carbonate solution and water and then dried with $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel with petroleum ether-dichloromethane gave a white product. Yield: 1.52 g (63%); MS (*m*/*z*): 806 (M^+).

9,9-Bis-(3-(9-phenyl-carbazoyl))-2,7-dipyrenylfluorene (DCDPF). Compound 1 (0.81 g, 1 mmol) and 1-pyrenyl boronic acid (0.75 g, 3 mmol), Pd $(PPh_3)_4$ (0.2 mmol), aqueous Na_2CO_3 (2.0 M, 4 mL), ethanol (2 mL), and toluene (10 mL) were mixed in a flask. The mixture was degassed and then refluxed for 24 h under a nitrogen atmosphere. After being cooled, the solvent was evaporated under vacuum and the product was extracted with dichloromethane (CH_2Cl_2). The CH_2Cl_2 solution was washed with water and dried with $MgSO_4$. Evaporation of the solvent, followed by column chromatography on silica gel with petroleum ether-dichloromethane gave a white product. The product was recrystallized from hexane-chloroform mixture to give the pure product. Yield: 0.81 g (77%); MS (*m*/*z*): 1048 (M^+). ^{1}HNMR ($CDCl_3$, 300 MHz): δ: 7.21(s, 2H), 7.32−7.42(m, 8H), 7.54−7.58 (m, 10H), 7.77−7.79 (d, 2H), 7.87−7.90 (d, 2H), 7.96−8.01 (t, 4H), 8.04−8.08 (m, 10H), 8.13−8.22 (m, 6H), 8.27 (s, 2H), 8.32−8.36 (d, 2H); MS (*m*/*z*): 1048 (M^+). Anal. Calcd For $C_{81}H_{48}N_2$: C, 92.72; H, 4.61; N, 2.67%. Found: C, 92.70; H, 4.60; N, 2.48%.

Measurements and OLEDs Fabrication. Absorption and fluorescence spectra were recorded respectively with a Perkin-Elmer Lambda 2S UV−vis spectrophotometer and a Perkin-Elmer LS50B Luminescence spectrophotometer. The highest occupied molecular orbitals (HOMO) values were measured directly by ultraviolet photoelectron spectroscopy (UPS), whereas the lowest unoccupied molecular orbital (LUMO) values were determined from the HOMO and positions of the lowest energy absorption edge of the UV absorption spectra.

Scheme 1. Synthetic Route of DCDPF



OLEDs were fabricated by vacuum deposition on ITO glass substrates with a sheet resistance of 30Ω/square. Before deposition, the ITO substrate was carefully cleaned, then dried in an oven at 120 °C, and finally treated with UV-ozone then loaded into a deposition chamber. The devices were fabricated by evaporating organic layers onto the ITO substrate sequentially at an evaporation rate of 2−4 Å/s and a pressure better than 5×10^{-6} mbar. The Mg:Ag alloy cathode was prepared by coevaporation of Mg and Ag at a volume ratio of 10:1. EL spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current−voltage−luminescence characteristics were measured with a computer-controlled Keithley 236 SourceMeter under ambient atmosphere.

Results and Discussion

The molecular structure and synthetic route of 9,9-bis-(3-(9-phenyl-carbazoyl))-2,7-dipyrenylfluorene (DCDPF) are shown in Scheme 1. The chemical structure of DCDPF was confirmed by ^{1}H nuclear magnetic resonance, mass spectrometry, and elemental analysis.

DCDPF is thermally stable up to 450 °C, as shown by its decomposition temperature determined from its Thermogravimetric Analyzer (TGA) measurement. No glass-transition temperature (T_g) can be observed in its differential scanning calorimertry (DSC) measurement. It indicates that DCDPF has good thermal stability. Figure 1 shows the absorption and fluorescence spectra of DCDPF in dilute dichloromethane solution and in solid film. The absorption spectrum in solution shows the characteristic vibration pattern of isolated fluorene and pyrene units. The photoluminescence (PL) spectrum of DCDPF in solution shows a deep blue emission peak centered at 423 nm. The fluorescence quantum yield of DCDPF in CH_2Cl_2 solution was measured to be 0.63 by calibrating against 9, 10-diphenylanthracene ($\phi_f \approx 0.90$) as a standard. The PL spectra in solution and in film are similar except for a red shift of 30 nm in the solid state.

To investigate the potential applications of DCDPF in OLEDs, a nondoped device with a typical three-layer structure of ITO/NPB (50 nm)/DCDPF (20 nm)/TPBI (30 nm)/LiF (0.5 nm)/MgAg (100 nm) was fabricated.

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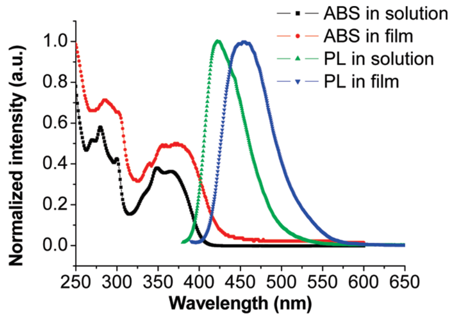

Figure 1. Absorption and emission spectra of DCDPF in solution and in film.

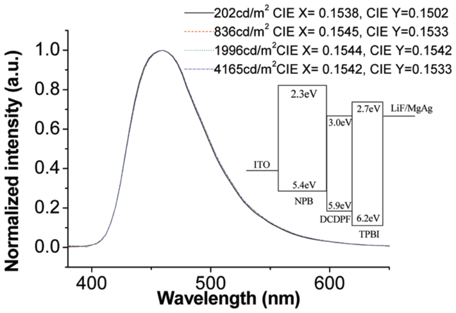

Figure 2. EL spectra of a DCDPF-based device emitting at different brightness levels.

In the device, ITO (indium tin oxide) and Mg:Ag are the anode and cathode, respectively; 4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl amino] biphenyl (NPB) is the hole-transporting layer (HTL), and 2,2′,2″- (benzene-1,3,5-triyl)−tris(1-phenyl-1H- benzimidazole) (TPBI) is the electron-transporting layer (ETL).

Figure 2 shows the electroluminescence (EL) spectra of the device at different brightness values. The device exhibits deep blue emission with a peak centered at 458 nm and CIE coordinates of (0.15, 0.15). The full width at half-maximum (fwhm) of the EL peak is only 71 nm. The EL spectrum of the device shows little difference (only about 5 nm red-shifted) from the corresponding PL spectrum in film, indicating that the EL emission originates from the singlet-excited states of DCDPF. Significantly, at luminance from 202 to 4165 cd/m^2 the spectra of the device are almost identical and CIE coordinates show little changes (from (0.154, 0.150) to (0.154, 0.153)). This suggests that the hole−electron recombination zone is well confined in the DCDPF layer over the wide range of operating voltage. This can be understood from the appropriate energy levels of DCDPF with respect to those of the neighboring layers, which are shown in the inset of Figure 2.

I−*V*−*L* characteristics of the DCDPF-based device are shown in Figure 3. The device shows a turn-on voltage (at a brightness of 1 cd/m^2) of <3.5 V and achieves a maximum brightness of 7332 cd/m^2 at a voltage of 9 V and a current density of 175 mA/cm^2.

Figure 4 shows current efficiency-current density-power efficiency characteristics of the device. The maximum current efficiency of the device is 4.4 cd/A (3.1 lm/W). It is known that the color purity and efficiency of blue OLEDs are often mutually compromised. Although many blue fluorescent emitters have been reported, high efficiency materials emitting in the deep-blue region are still rare. Performance of DCDPF device with a maximum efficiency of 4.4 cd/A (3.1 lm/W) and CIE coordinates of (0.15, 0.15) are among the best values ever reported for nondoped deep blue fluorescence OLEDs. Significantly, the current efficiency shows only a mild decrease as the current density increases, and a high efficiency of 4.2 cd/A can still be obtained at a current density of 175 mA/cm^2.

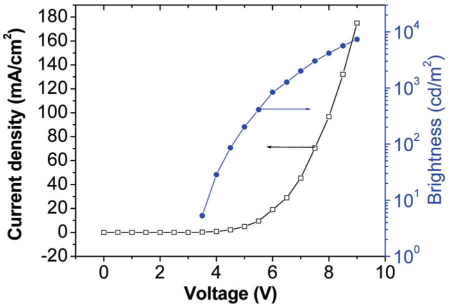

Figure 3. Current density−voltage−brightness curves of the device. Inset is the energy level of the device.

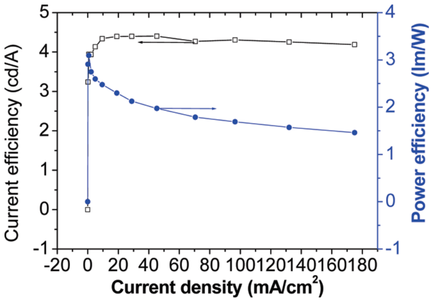

Figure 4. Current efficiency−current density−power efficiency characteristics of the device.

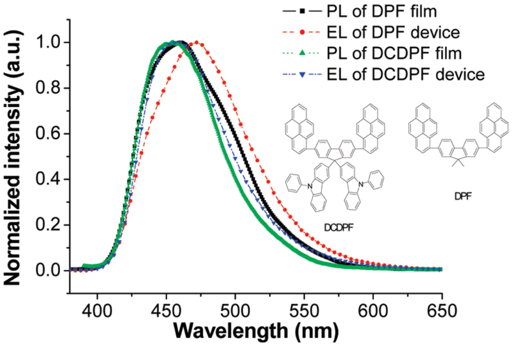

Figure 5. PL of DCDPF and DPF films and EL spectra of their corresponding devices.

In our previous report, a nondoped OLED using 9,9-dimethyl-2,7-dipyrenylfluorene (DPF) as the host emitter shows highly efficient blue emission with a peak centered at 468 nm and CIE coordinates of $x = 0.15$, $y = 0.19$.[23] The molecular structures of DPF and DCDPF are shown in the inset of Figure 5. DCDPF has a similar chemical

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Table 1. Important Data of PL and EL of DPF and DCDPF

	PL (nm) (solution)	PL (nm) (film)	fwhm (nm)	EL (nm)	fwhm (nm)	CIE (x, y)	HOMO/LUMO eV
DCDPF	423	453	68	458	71	0.15, 0.15	5.9/3.0
DPF	421	460	81	468	84	0.15, 0.19	5.7/2.7

structure as DPF except for the different substituents at the 9-position of fluorene. Table 1 lists the key data about DPF and DCDPF for comparison. The PL spectra of their films and EL spectra of their devices are also shown in Figure 5. Although the PL spectra of DCDPF and DPF in solution are similar, significant difference can be seen in the PL spectra of their solid films. The PL spectrum of DCDPF film is much narrower than that of DPF film. The full width at half-maximum (fwhm) of the PL spectrum of DCDPF film is only 68 nm, which is much lower than that of DPF (81 nm). It indicates that introduction of the bulky carbazole units at the 9-position of fluorene would reduce the formation of aggregates emitting at longer wavelength. This leads to the better blue emission of DCDPF device than DPF device. The EL spectrum of DCDPF-based device is thus much narrower and 10 nm blue-shifted comparing to that of the DPF-based device. Thus, the CIE coordinates of DCDPF-based device ($x = 0.15$, $y = 0.15$) is much better than that of DPF-based device ($x = 0.15$, $y = 0.19$). Due to the compromise between efficiency and color purity in blue OLEDs, the efficiency of DCDPF device (4.4 cd/A, 2.3 lm/W) at 20 mA/cm^2 is lower than that of DPF device (5.9 cd/A, 2.9 lm/W) after improvement in color purity.

In summary, a new blue emitter, 9,9-bis-(3- (9-phenyl-carbazoyl))-2, 7-dipyrenylfluorene (DCDPF) has been synthesized and characterized. OLED based on DCDPF in a nondoped device structure exhibits deep-blue emission with a peak centered at 458 nm and CIE coordinates of (0.15, 0.15). The maximum efficiency of the blue OLED is 4.4 cd/A (3.1 lm/W). The results indicate that introducing carbazole units at the 9-position of fluorene is an efficient means for reducing red shift of the emission caused by molecular aggregation.

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