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Blue Organic Light-Emitting Diodes Based on Triphenylene Derivatives

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A series of blue fluorescent emitters based on triphenylene derivatives were synthesized *via* the Diels -Alder reaction in moderate yields. The electronic absorption and emission characteristics of the new functional materials were affected by the nature of the substituent on the triphenylene nucleus. Multilayered OLEDs were fabricated with a device structure of: ITO/NPB (50 nm)/EML (30 nm)/Bphen (30 nm)/Liq (2.0 nm)/Al (100 nm). All devices showed efficient blue emissions. Among those, a device using **1** gives the best performances with a high brightness (978 cd m^{-2} at 8.0 V) and high efficiencies (a luminous efficiency of 0.80 cd/A, a power efficiency of 0.34 lm/W and an external quantum efficiency of 0.73% at 20 mA/cm^2). The peak wavelength of the electroluminescence was 455 nm with CIE*x*,*y* coordinates of (0.17, 0.14) at 8.0 V.

Key Words : OLED, Blue fluorescence, Triphenylene derivatives

Introduction

In recent years, organic light-emitting diodes (OLEDs) have attracted considerable attention due to their potential applications in full-color, flat-panel displays and space illumination.[1] Red, green, and blue primary emitters are needed to produce full-color OLEDs for displays or lighting. High efficiency and saturated color have been achieved for red and green light-emitting materials.[2] However, blue devices require further improvement in their efficiency and color index. In particular, a highly efficient, pure deep-blue-emitting material with a Commission International de l'Éclairage *y* coordinate value (CIE *y*) of < 0.15 needs to be developed to reduce OLED power consumption and increase the color range.[3] However, it is difficult to design deep-blue-emitting materials with high efficiency, saturated color purity, and long operation times due to the wide band-gap of blue materials. Although many blue light-emitting materials based on pyrene,[4] anthracene,[5] fluorenes,[6] aromatic hydrocarbon,[7] and triarylamine[8] derivatives have been reported, the EL efficiencies of these deep-blue OLEDs are rather poor compared to those of sky-blue OLEDs. Therefore, the search for new efficient deep-blue fluorescent materials with high performance remains a major challenge.

In this study, we have designed and synthesized a new class of blue emitters based on triphenylene derivatives. These triphenylenes belong to the group of PAH (polycyclic aromatic hydrocarbon) compounds, which have the good electrical properties and photophysical properties caused by their conjugated hydrocarbon structure.[9] Herein, we describe the synthesis and electroluminescent properties of highly efficient blue-emitting materials (**1-3**) based upon triphenylene derivatives for OLED applications.

Experimental

Material Preparation and Characterization. Unless stated otherwise all solvents were dried using standard procedures and all reagents were used as received from commercial sources. All reactions were performed under a N_2 atmosphere. Compounds phencyclone (**a**),[10] 2,7-diethynyl-9,9-dimethyl-9*H*-fluorene (**b**),[11] 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (**c**)[12] was previously reported.

^{1}H and ^{13}C NMR spectra were recorded on a Varian (Unity Inova 300Nb or Unity Inova 500Nb) spectrometer. FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Elemental analysis (EA) was measured using an EA 1108 spectrometer.

General Procedure for the Diels-Alder Reaction: 1,2,4-Trimethylbenzene (25 mL) was added to a mixture of phencyclone (1.0 g, 1.25 mmol) and 1,4-diethynylbenze (0.15 g, 1.19 mmol) in a flask, and heated under reflux at 180 °C for 48 h. The reaction mixture was filtered by EtOH. The crude solid dissolved in toluene was filtered, and evaporated under reduced pressure. The crude product was then recrystallized from tetrahydrofuran/EtOH.

1,4-Bis(1,4-diphenyltriphenylen-2-yl)benzene (1): (69% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.1 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (s, 2H), 7.54-7.50 (m, 6H), 7.46-7.34 (m, 12H), 7.14-6.99 (m, 12H), 6.90 (s, 4H); FT-IR [ATR]: ν = 3060, 3018, 1441, 845, 730, 695 cm^{-1}; Anal. calcd for $C_{66}H_{42}$: C 94.93, H 5.07; found: C 94.67, H 5.33%.

2,2'-(9,9-Dimethyl-9*H*-fluorene-2,7-diyl)bis(1,4-diphenyltriphenylene) (2): (71% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.8 Hz, 4H), 7.76 (s, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.64-7.53 (m, 8H), 7.47-7.39 (m, 10H), 7.32 (d, *J* = 9.6 Hz, 2H), 7.16-7.10 (m, 12H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.76 (s, 2H), 0.92 (s, 6H); FT-IR [ATR]: ν = 3057, 3031, 2957, 2922, 2856, 1467, 1441, 825, 762, 701 cm^{-1}; Anal. calcd for $C_{75}H_{50}$: C 94.70, H 5.30; found: C 94.60, H 5.40%.

1,4-Bis(2',3',4',5'-tetraphenylbenzen-1-yl)benzene (3): (65% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.14 (s, 8H), 6.93-6.90 (m, 14H), 6.86-6.75 (m, 22H); FT-IR

[ATR]: ν = 3055, 3022, 2937, 2865, 1599, 1440, 1071, 843, 759, 697 cm^{-1}; Anal. calcd for $C_{66}H_{46}$: C 94.34, H 5.66; found: C 94.67, H 5.33%.

Photophysical Measurements. The UV-Vis absorption measurements of these compounds in dichloromethane (10^{-5} M) were acquired with a Sinco S-3100 in a quartz cuvette (1.0 cm path). Photoluminescence spectra were measured on an Amincobrowman series 2 luminescence spectrometer. The fluorescence quantum yields of the blue materials were determined in dichloromethane at 293 K against DPA as a reference (Φ = 0.90).[13]

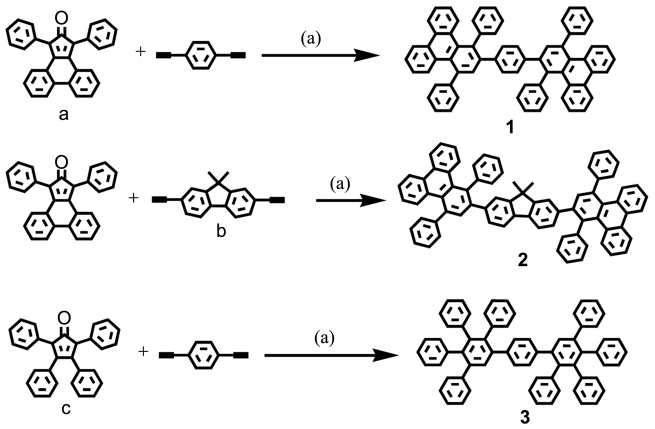
HOMO (highest occupied molecular orbital) energy levels were determined with a low energy photoelectron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. LUMO (lowest unoccupied molecular orbital) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

Device Fabrication and Measurements. OLED fabrication of the indium-tin-oxide (ITO) thin films coated on glass substrates were used, which were 12 Ω/square of the sheet resistivity and a 1000 Å of thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: acetone, methyl alcohol, distilled water, followed by storage in isopropyl alcohol for 20 min and drying with a N_2 gas gun. The substrates were treated with O_2 plasma Ar environment. Organic layers were deposited by thermal evaporation from resistively heated alumina crucibles onto the substrate at a rate of 1.0 Å/s. All organic materials and metal were deposited under high vacuum (5.0×10^{-7} Torr). The OLEDs were fabricated in the following sequence: ITO (Indium tin oxide)/4,4'-bis(*N*-(1-naphthyl)-*N*-phenylamino)-biphenyl (NPB, HTL) (50 nm)/Blue materials **1-3** (30 nm)/ 4,7-diphenyl-1,10-phenanthroline (Bphen, ETL) (30 nm)/ lithium quinolate (Liq) (1.0 nm)/Al (100 nm). Current-voltage-luminance (*J-V-L*) characteristics and electroluminescence (EL) spectra of the devices were measured with a Keithley 2400 source measurement unit and CS 1000A spectrophotometer.

Results and Discussion

The molecular structures and synthetic routes of the newly designed triphenylene derivatives **1-3** are illustrated in Scheme 1.

The triphenylene derivatives **1-3** were prepared by Aldol condensation reaction and the subsequent Diels-Alder reaction with moderate yields in the range of 60-75 %.



Scheme 1. Structures and Synthetic routes for blue fluorescent materials **1-3**. Reagents: (a) 1,2,4-Trimethylbenzene, reflux at 180 °C, 48 h.

To examine the photophysical properties of triphenylene derivatives **1-3**, the UV/Vis absorption and photoluminescence (PL) studies were carried. Figure 1 shows the absorption and emission spectra of blue materials **1-3** and their photophysical data are summarized in Table 1. Compared to material **1**, the UV-vis and PL spectra of material **2** were slightly red-shifted due to the extended π-conjugation. However, the UV-vis and PL spectra of material **3** showed the blue-shifts by 40 and 46 nm, respectively, due to an interruption of the π-conjugation of compound **3** by the cleavaged triphenylene core moiety.

The highest occupied molecular orbital (HOMO) levels were measured using a photoelectron spectrometer (Riken-Keiki AC-2) and the lowest unoccupied molecular orbital (LUMO) levels were calculated by subtracting the corresponding optical band gap energies from the HOMO values. The HOMO energy levels of materials **1-3** were estimated to be –6.01, –6.00 and –6.11 eV, respectively. The optical energy band gaps (Eg) for these materials were 3.37, 3.29 and 3.80 eV, respectively, as determined from the absorption spectra. The LUMO energy levels of materials **1-3** were calculated to be –2.64, –2.71 and –2.31 eV, respectively, by subtracting the optical band gaps from the HOMO energy levels. Figure 2 shows the HOMO and LUMO energy levels of blue fluorescent materials **1-3**, along with the other materials used in OLED devices.

To explore the electroluminescent properties of blue

Table 1. Photophysical data for the compounds **1-3**

Compound	UV_{max}[a] [nm]	PL_{max}[a,b] [nm]	FWHM [nm]	HOMO[e]	LUMO[e]	Eg[d]	Φ[c]
1	294	406/400	52	6.01	2.64	3.37	0.13
2	295	410/406	58	6.00	2.71	3.29	0.33
3	254	360/361	61	6.11	2.31	3.80	0.76

[a]Maximum absorption and emission wavelength, measured in CH_2Cl_2 solution. [b]Measured in the film [c]Φ_f's were determined in a CH_2Cl_2 solution at 298 K against DPA as a reference (Φ = 0.90). [d]ΔE is the band-gap energy estimated from the intersection of the absorption and photoluminescence spectra. [e]HOMO energy level was determined by low-energy photoelectron spectrometer (Riken-Keiki, AC-2) and LUMO = HOMO + ΔE

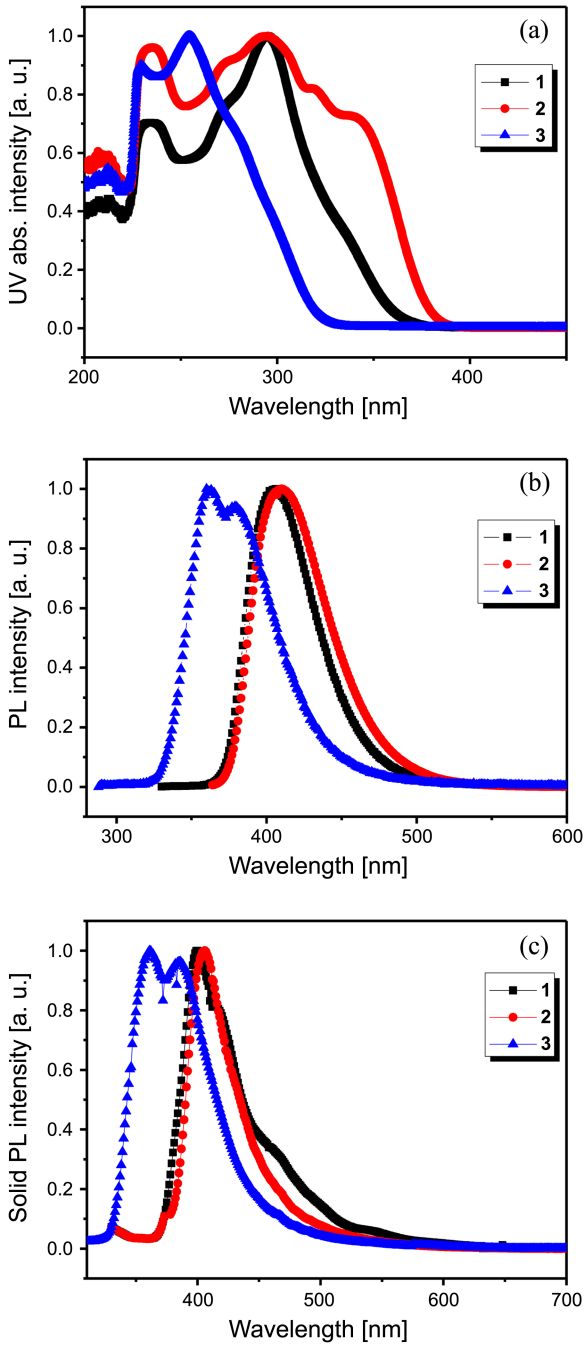


Figure 1. (a) UV-vis absorption spectra, (b) PL spectra in CH_2Cl_2 and (c) PL spectra in thin films of blue emitters **1-3**.

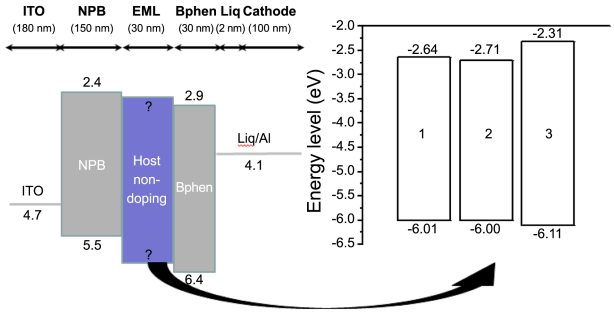


Figure 2. Energy levels of the materials used in the devices.

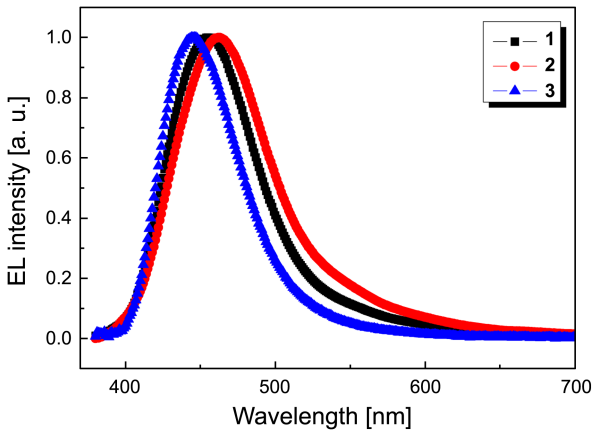


Figure 3. EL spectra of devices **1-3**.

fluorescent materials **1-3**, OLED devices with the following configuration: ITO/4,4'-bis(*N*-(1-naphthyl)-*N*-phenylamino)-biphenyl (NPB) (50 nm)/Blue materials **1-3** (30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm)/lithium quinolate (Liq) (2.0 nm)/Al (100nm) were fabricated and their electroluminescent properties are summarized in Table 2. Figure 3 shows the normalized EL spectra of the devices **1-3**. All devices exhibited an efficient blue emission with maximum emission peaks of 445-462 nm, which are well compatible with the PL spectra of materials **1-3**. Interestingly, compared to the PL spectra of materials **1-3**, the EL spectra showed the large red-shifts by around 50 nm. Presumably, the differences in solvation between solution state and solid state device would contribute to the large differences in the maximum peaks of PL and EL spectra. The CIE*x,y* coordinates of devices **1-3** were (0.17, 0.14), (0.17, 0.17) and (0.16, 0.09) at 8.0 V, respectively. Among devices **1-3**, device **3** shows the most pure deep blue emission with the CIE*x,y* coordinates of (0.16, 0.09), which is close the standard deep blue emission. Figure 4 shows current density-voltage-luminance (*J-V-L*), the luminous effi-

Table 2. EL performance characteristics of devices **1-3**

Device	EL_{max} [nm]	L [cd/m^2][a]	LE [cd/A][b/c]	PE [lm/W][b/c]	EQE [%][b/c]	CIE (*x,y*)[d]
1	455	978	0.86/0.80	0.52/0.34	0.74/0.73	(0.17,0.14)
2	462	430	0.75/0.63	0.43/0.23	0.55/0.48	(0.17,0.17)
3	445	265	0.46/0.39	0.19/0.11	0.61/0.48	(0.16,0.09)

Device (ITO/NPB/host **1-3**/Bphen/Liq/Al). [a]Maximum luminance at 8.0 V. [b]Maximum values. [c]At 20 mA cm^{-2}. [d]Commission Internationale l'Énclairage (CIE) coordinates at 8.0 V.

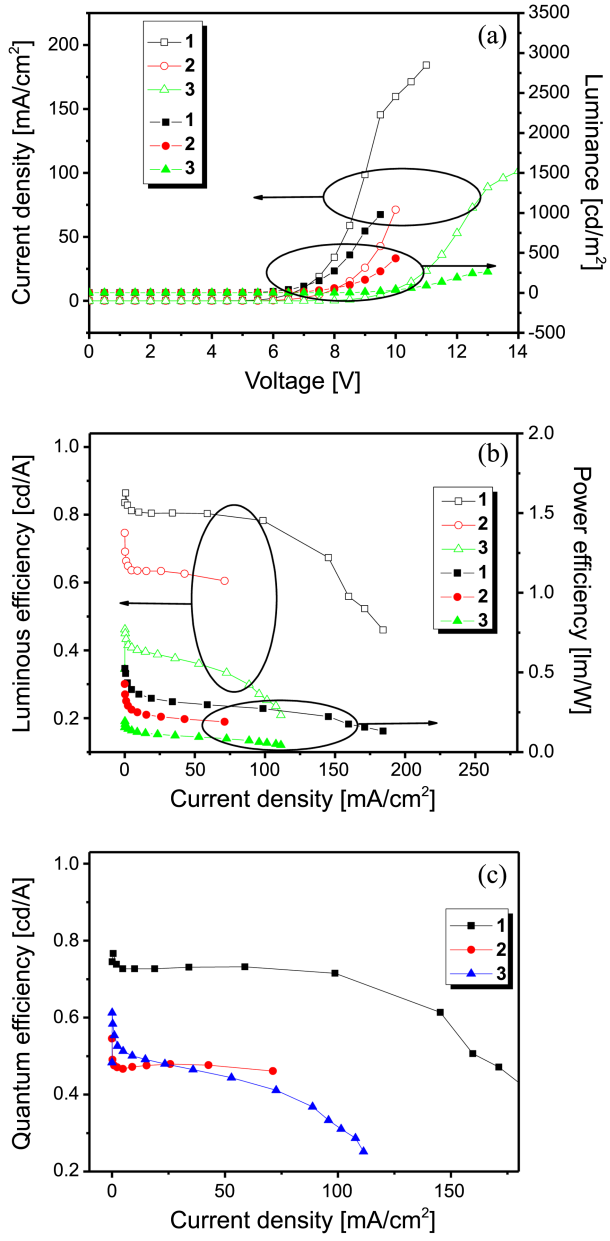


Figure 4. (a) *J-V-L*, (b) luminous and power efficiencies, and (c) external quantum efficiencies of the devices **1-3** as a function of current density.

ciencies, power efficiencies and external quantum efficiencies (EQE) as a function of current density for devices **1-3**. Among the devices **1-3**, the sky-blue device **1** exhibits the outstanding EL performances with its maximum luminous, power and external quantum efficiencies of 0.86 cd/A, 0.52 lm/W, and 0.74% (0.80 cd/A, 0.34 lm/W, and 0.73% EQE at 20 mA/cm^2), with CIE*x*,*y* coordinates of (0.17, 0.14) at 8.0 V, respectively. However, a deep-blue device **3** showed the low EL efficiencies with a maximum luminous, power and external quantum efficiencies of 0.46 cd/A, 0.19 lm/W, and 0.61% (0.39 cd/A, 0.11 lm/W, and 0.48% at 20 mA/cm^2) with the color coordinate of (0.16, 0.09) at 8.0 V, respectively.

Compared to material **1**, the higher LUMO energy level and the lower HOMO level of material **3** would prevent the effective electron and hole injection into the emitting layer of device **3** in comparison with device **1**. These ineffective carrier injection properties of device **3** would lead the reduced EL efficiencies of device **3**.[14] Although materials **1** and **2** have the similar HOMO/LUMO energy levels and thus similar hole and electron injection properties, devices **1** showed the improved EL efficiencies in comparison with device **2**. Presumably, the other factors such as carrier mobility and carrier recombination factor would contribute the differences in EL efficiencies of devices **1** and **2**.

Conclusions

A series of fluorescent materials **1-3** based on triphenylene were synthesized *via* Diels-Alder reaction. Organic light-emitting devices (OLED) has been fabricated to investigate their electroluminescent properties. A device using 1,4-bis(1,4-diphenyltriphenylen-2-yl)benzene (**1**) as the emissive layer exhibited the outstanding EL performances with its maximum luminous, power, and external quantum efficiencies of 0.86 cd/A, 0.52 lm/W, and 0.74% (0.80 cd/A, 0.34 lm/W, and 0.73% EQE at 20 mA/cm^2), with CIE*x*,*y* coordinates of (0.17, 0.14) at 8.0 V, respectively. This study demonstrated that the new triphenylene derivatives are promising blue emitting materials for developing high-efficiency OLEDs.

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