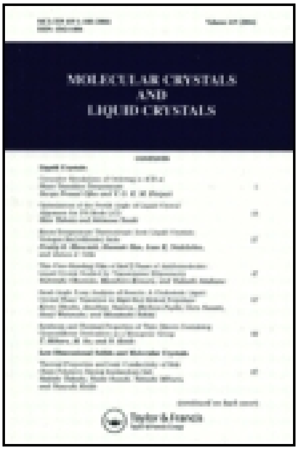

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New Multi-Phenylated Carbazole Derivatives for OLED through Diels-Alder Reaction

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New Multi-Phenylated Carbazole Derivatives for OLED through Diels-Alder Reaction

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We synthesized multi-phenylated carbazole derivatives such as 3,6-Bis[(2,3,4,5-tetraphenyl)phenyl]-9-ethylcarbazole(BTPEC) and 3,6-Bis(7,10-diphenyl-fluoranthene)-9-ethlycarbazole(BDPEC), through Diels-Alder reaction. These products were identified by NMR, Fab-Mass analysis.

Electro-optical properties of these materials were characterized by cyclic voltammetry (CV) and, UV-visible and photoluminescence (PL) spectra. The maximum absorbance of BTPEC appeared at 307 nm and BDPEC showed maximum absorbance of 307 nm and 388 nm. And two compounds also exhibited PL peaks at 389 nm and 483 nm. When we used these two materials as hole injection layer(HIL) and hole transport layer(HTL) in OLED device, the devices showed about 3 cd/A and 2 cd/A, respectively.

Keywords: Diels-Alder reaction; electroluminescent; hole injection; hole transport; organic light-emitting diode

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INTRODUCTION

Organic light-emitting diodes (OLEDs) based on organic molecules are currently the subject of an intense research effort due to their promise as devices for full-color large display applications [1–2]. Recently, a star-burst amine 4,4′,4″-tris{N,(3-methylphenyl)-N-phenylamino}-triphenylamine(m-MTDATA)[3], 4,4′,4″-tris{N,-(2-naphthyl)-N-phenylamino}-triphenylamine (2-TNATA) [3] and copper phthalocyanine (CuPc) [4] compounds acting as a hole injection layer(HIL) in OLED device, have been inserted between hole transporting layer(HTL) and the transparent anode such as ITO in order to improve device performance.

Unfortunately, CuPc absorbs slightly blue and red light and m-MTDATA has disadvantage of low T_g as 75°C [5,6]. This issues make kind of limitation to apply materials to device.

Our group have firstly synthesized several kinds of multiphenylated compound by using Diels-Alder reaction [7,8]. Recently, Gelsen et al. reported multiphenylated compounds as a HTL in OLED device [9].

In this study, we synthesized 3,6-Bis[(2,3,4,5-tetraphenyl)phenyl]-9-ethylcarbazole(BTPEC) and 3,6-Bis(7,10-diphenyl-fluoranthene)-9-ethlycarbazole(BDPEC), as multi-phenylated carbazole derivatives by using Diels-Alder reaction. Electro-optical properties of these materials were characterized by cyclic voltammetry(CV) and, UV-visible and photoluminescence (PL) spectra. Multilayered EL devices were fabricated using these materials as a hole injection layer (HIL), hole transport layer (HTL).

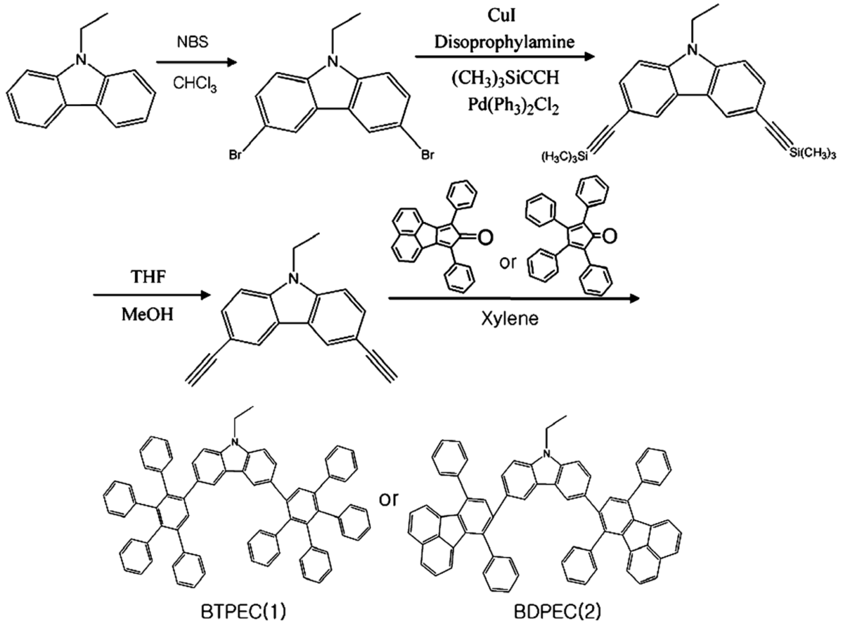
EXPERIMENTAL

Synthesis

3,6-Bis[(2,3,4,5-tetraphenyl)phenyl]-9-ethylcarbazole(BTPEC)

9-ethyl-3,6-diethnyl-9H-carbazole(1 g, 4.1 mmol) and 2,3,4,5-tetraphenyl cyclopenta-2,4-dienone(3.47 g, 9.04 mmol) were added to dried xylene solvent (100 ml). This mixture was heated to 120°C for 12 hr until no ejecting CO gas. After the reaction mixture cooled, the solution was evaporated. The residue was dissolved in $CHCl_3$ and ethanol. And the residue was purified by column chromatography with EA: n-Hexane(1:10) eluent to afford white solid(1.13 g, 28%) (Scheme 1).

^1H NMR($CDCl_3$) δ: 7.89 (s, 2H), 7.67 (s, 2H), 7.17–6.80(m, 44H), 4.21(q, 2H), 1.34(t, 3H)/Fab^+-Mass m/e: 956



SCHEME 1 Synthetic route of BTPEC(1) and BDPEC(2).

3,6-Bis(7,10-diphenyl-fluoranthene)-9-ethlycarbazole(BDPEC)

9-ethyl-3,6-diethnyl-9H-carbazole (0.83 g, 3.41 mmol) and 7,9-diphenyl-8H-cyclopenta[α] acenaphthylen-8-one(DPCPA)(2.68, 7.52 mmol) were added to dried xylene solvent (100 ml). DPCPA was synthesized by knoevenagel reaction using dione and carbonyl derivatives. This mixture was heated to 120°C for 12 hr. After the reaction mixture cooled, the solution was evaporated. The residue was dissolved in $CHCl_3$ and ethanol. And the residue was purified by column chromatography with EA: n-Hexane(1:10) eluent to afford yellow solid(0.907 g, 29%)(Scheme 1).

^1H NMR($CDCl_3$) δ: 7.92 (s, 2H), 7.77–7.12(m, 32H), 6.68(d, 2H), 6.66(d, 2H), 4.22(t, 2H), 1.35(q, 3H)/Fab$^+$-Mass m/e: 900

Fabrication of OLEDs

For EL device, BTPEC and BDPEC were vacuum-deposited on top of ITO(1200 Å/30 ohm) under 10^{-6} torr, the rate of deposition being 1 Å/sec to give an emitting area of 4 mm^2 and other organic layer and aluminum layer were continuously deposited with same vacuum condition. Current-voltage (I–V) characteristics of the fabricated

OLEDs were measured using Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-1000.

MEASUREMENT

^{1}H NMR spectra were recorded on a Brucker, Advance DPX-300. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 seris II. The optical absorption spectra were measured by a HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50(Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. Redox potential of the compounds were determined by cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of $30 \sim 200\,\text{mV/s}$. The compound of interest was dissolved in N,N-Dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated $Ag/AgNO_3$ referenced electrode. Ferrocene was used for potential calibration (all reported potentials are referenced against ferrocene/ferrocenium, FOC) and for reversibility criteria.

RESULT AND DISCUSSION

As shown in Scheme 1, the present compounds consist of carbazole group, which is good hole transporting moiety, and multiphenylated rings. In order to avoid excimer and intermolecular overlapping effect we also attached ethyl group to carbazole in core site.

The motivation for introducing fluoranthene instead of tetraphenyl moiety in BDPEC compound is that we try to compare the electrical and optical effect of multiphenylated compound and fused ring compounds.

These products were finally purified with silica column method to have highly pure powder and were identified by NMR, Fab-Mass analysis.

Figure 1 shows UV-visble spectra of BTPEC and BDPEC films on glass. The maximum absorbance of BTPEC appeared at 307 nm and BDPEC showed maximum absorbance of 307 nm and 388 nm. BDPEC contains fused ring of fluoranthene and it extends the conjugated length and causes absorbance of 388 nm. BTPEC and BDPEC can be applied to HIL or HTL layer due to no absorption at visible light region although BDPEC absorbed slightly light at region of 400 nm to 450 nm. BTPEC exhibited PL maximum value of 389 nm but no visible PL light by naked eye. BDPEC showed green PL light of 483 nm.

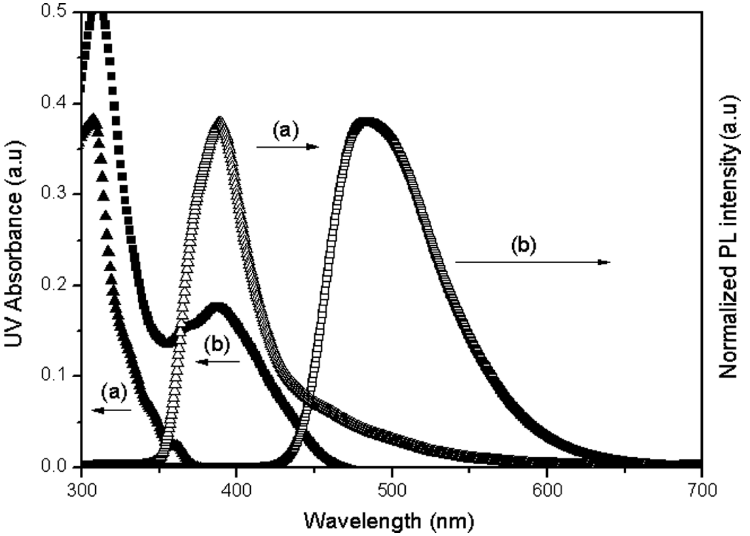


FIGURE 1 UV-visible (Solid) and PL (Open) spectra of BTPEC(a)(triangle) and BDPEC(b)(square) films on glass.

We fabricated OLED device including the present compounds as HIL layer and EL performance was summarized in Table 1. As shown in Table 1, there was no changed EL maximum values and CIE values of Alq3 emitter in OLED device which included the present compounds as HIL layer.

The devices emitted normal green light of Alq3 with (0.30, 0.52) CIE value and showed good EL efficiency of 2.6 to 3.1 cd/A.

When we fabricated OLED device using 2-TNATA as a hole injection layer which is commercialized, the device showed turn on voltage of 6 V, power efficiency of 2.37 lm/w. Although operating voltage of our

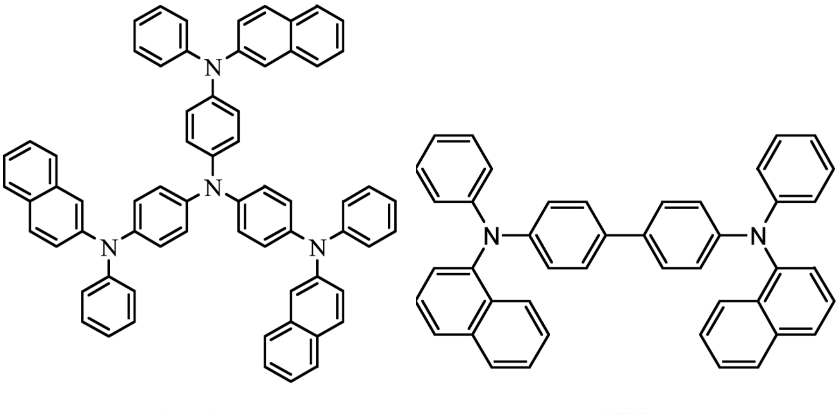
TABLE 1 Performance of HIL in Multi-Layered Device: ITO/BTPEC or BDPEC(60 nm)/NPB(15 nm)/Alq3(70 nm)/LiF(1 nm)/Al device

	Current density (mA/cm^2)	Voltage (V)	Brightness (cd/m^2)	CIE	Efficiency (cd/A)	Efficiency (lm/W)
BTPEC	10.00	23.0	306	(0.305,0.522)	3.06	0.42
	25.00	26.0	652	(0.304,0.520)	2.61	0.31
BDPEC	10.00	19.0	286	(0.304,0.529)	2.86	0.47
	25.00	20.7	741	(0.304,0.528)	2.96	0.45

TABLE 2 Electronic Levels of BTPEC and BDPEC

	HOMO (eV)	LUMO (eV)	Band gap (eV)
BTPEC	5.53	2.19	3.34
BDPEC	5.50	2.69	2.81

device was higher and power efficiency(lm/w) was relatively lower compared to 2-TNATA device's, we believe that the present compounds have good hole transporting property because of high luminescence efficiency in Table 1. As shown in Table 2, HOMO levels of BTPEC and BDPEC are located at the lower level of ITO work function. And LUMO level of BTPEC showed 2.19 eV, which means that it may play a role of electro-blocking effect in OLED device. Based on CV data and UV-visible on-set point, we could get HOMO and LUMO levels although it is not absolute value due to relative experimental method. The LUMO level of commercialized hole injection and hole transporting materials of 2-TNATA and NPB (see Scheme 2.) was reported as 2.18 eV and 2.3 eV [10]. The reason why our device showed higher operating voltage of over 20 V is that HOMO levels of the compounds were not matched with NPB's HOMO level of 5.4 eV.



2-TNATA NPB

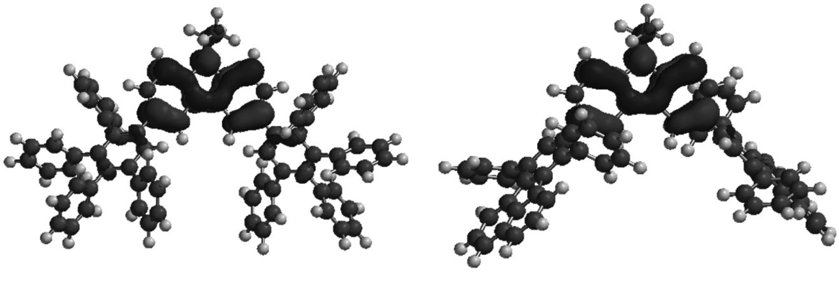
SCHEME 2 Chemical structures of 4,4′,4″-tris(N-(2-naphthyl)-N-phenylamino)-triphenylamine (2-TNATA) and N,N′-di(nphthalen-1-yl-N,n′-diphenylbenzidine(NPB).

TABLE 3 Performance of HTL in Multi-Layered Device: ITO/2-TNATA (60 nm)/BTPEC or BDPEC(15 nm) /Alq_3(70 nm)/LiF(1 nm)/Al device

	Current density (mA/cm^2)	Voltage (V)	Brightness (cd/m^2)	CIE	Efficiency (cd/A)	Efficiency (lm/W)
BTPEC	10.00	9.4	185	(0.290,0.471)	1.85	0.62
	25.00	10.5	497	(0.294,0.481)	1.99	0.59
BDPEC	10.00	6.3	195	(0.353,0.480)	1.95	0.97
	25.00	7.3	490	(0.342,0.479)	1.96	0.85

We also used these compounds as HTL materials and summarized EL data in Table 3. EL luminescence efficiency was 1.9 to 2.0 cd/A, but power efficiency(lm/w) was slightly increased to 0.6 to 1.0 lm/w compared to the previous device data(Table 1) due to removing the dismatched electronic levels between synthetic compounds and NPB.

In order to compare the structure and property of BTPEC and BDPEC, we have also calculated HOMO levels of the present compounds by using Semi-Empirical/AM-1 method as shown in Figure 2. Both of electron density are mainly located at carbazole group and it is not largely effected by fused ring side group instead of tetraphenylated moiety. However, BDPEC showed slightly increased EL property of 1.95 cd/A and 0.97 lm/w. It might be explained by that fused ring side group is effective to show better hole transporting and injection property compared to 4-phenylated phenyl group.



(a) BTPEC (b) BDPEC

FIGURE 2 HOMO levels of BTPEC and BDPEC calculated at the Semi-Empirical/AM-1 using Spartan'04 for Windows.

CONCLUSION

We have synthesized new multi-phenylated carbazole derivatives BTPEC and BDPEC through Diels-Alder reaction with wide band gap. Alq3 OLED device including BTPEC HIL material showed 3.1 cd/A luminescence efficiency and Alq3 OLED device having BDPEC HTL material exhibited 1 lm/W power efficiency. Further studies on new OLED device configuration as well as phosphorescent host system are underway.

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