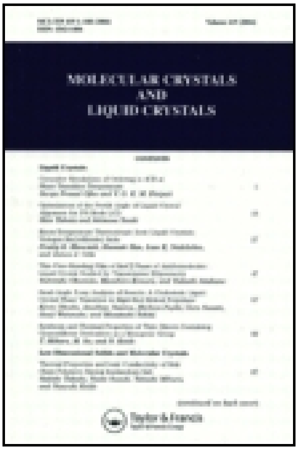

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New Blue and Bluish Green Electroluminescent Properties of Fully Substituted Ethylene Moieties

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New Blue and Bluish Green Electroluminescent Properties of Fully Substituted Ethylene Moieties

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We synthesized 1,1,2,2-tetrakis(4′-tert-butylbiphenyl)ethene[TBBPE] and 1,2-di(4′-tert-butyl-phenyl)-1,2-bis(4′-tert-butyl-biphenyl) ethene [BPBBPE]. TBBPE and BPBBPE film showed PL maximum value of 489 nm and 511 nm due to longer conjugation length of TBBPE. In EL device, TBBPE device showed slightly better I-V curve than BPBBPE's because there is lower energy barrier between Alq_3 *and TBBPE's LUMO levels. We observed luminance efficiency of 1.87 cd/A with blue color as (0.177, 0.249) CIE value in BPBBPE emitting system and 4.44 cd/A with (0.240, 0.435) CIE value in TBBPE device.*

Keywords: blue emitting material; electroluminescence; McMurry reaction; tetra substituted ethylene

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 [1–3], numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence (EL), from red, to green, to blue [4–6].

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Although considerable research efforts have been carried out to enhance the performance suitable for practical use, however, a lot of problems to solve still remain, for example blue emitting material, the device lifetime and the luminous efficiency, etc.

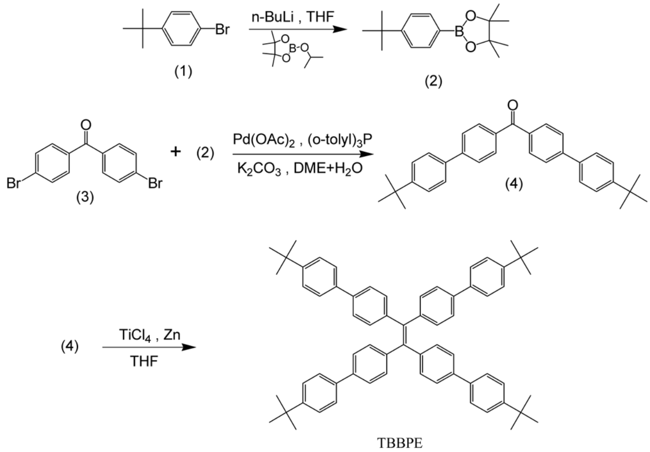
For instance, 4,4′-bis(2,2-diphenylvinyl)-1,1′-biphenyl (DPVBi) shows excellent EL performance but it also exhibits low glass transition temperature (T_g) of 64°C [7] and makes defect due to recrystalization during device operation. In order to overcome this issue, new chemical structures of diarylanthracene, di(styryl)arylene, fluorene and pyrene have been studied [8].

In this work we synthesized blue emitting materials using new chemical structure concept of fully substituted ethylene moieties. Double-layered and multi-layered EL devices were fabricated with synthesized material and evaluated in terms of emission color and luminescence efficiency.

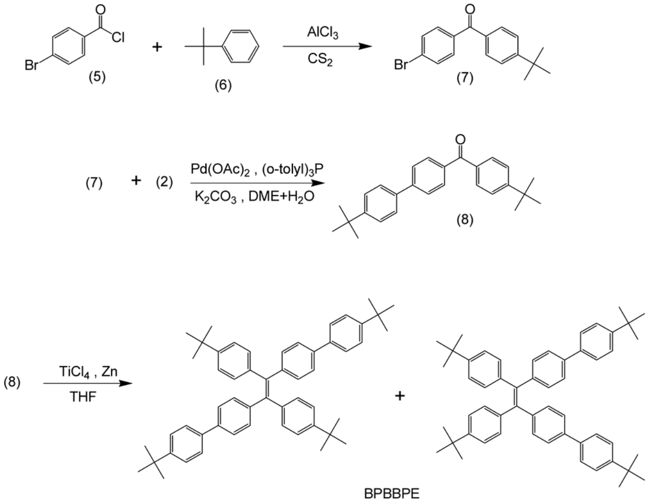
EXPERIMENTAL

Synthesis

Synthesis of 1,1,2,2-tetrakis(4′-tert-butylbiphenyl)ethene[TBBPE] and (E)or(Z) 1,2-di(4′-tert-butyl-phenyl)-1,2-bis(4′-tert-butyl-biphenyl) ethene [BPBBPE]. TBBPE and BPBBPE in Schemes 1, 2 were obtained by McMurry reaction as below. Bis(4′-tert-butylbiphenyl)methanone(4)(2 g, 4.5 mmol), Zn-powder(0.7 g, 11.25 mmol) were added to dried THF solvent(150 ml), then $TiCl_4$(1 ml, 9 mmol) were added into the



SCHEME 1 Synthetic route of TBBPE.



SCHEME 2 Synthetic route of BPBBPE.

reaction mixture. The mixture was heated to 60°C for 1 hr under nitrogen. After the reaction mixture cooled, and extracted with diethylether. The organic layer was dried by anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was dissolved in $CHCl_3$ and added to methanol in order to get pure solid. The precipitate was filtered and washed with methanol. Yellowish powder was purified by column chromatography with $CHCl_3$: n-hexane (1:1) eluent to afford white solid(TBBPE) (1.3 g, 67%).

^{1}H NMR: δ: 7.16(d, 8H), 7.37(d, 8H), 7.42(d, 8H), 7.51(d, 8H), 1.34 (s, 36H).

BPBBPE was obtained by using (4-tert-butylphenyl)(4′-tert-butylbiphenyl) methanone (8) (2 g, 5.4 mmol) as McMurry reaction. (1.2 g, 63%).

^{1}H NMR δ: 7.50(q, 4H), 7.415(q, 4H), 7.335(q, 4H), 7.11(q, 4H), 7.08(q, 4H), 6.97(q, 4H), 1.32 (s, 18H), 1.29 (s, 18H).

Fabrication of OLED

For EL device, TBBPE and BPBBPE were vacuum-deposited on top of 2-TNATA (500 Å)/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.

RESULTS AND DISCUSSION

These products were finally purified with recrystallization and silica column method to have highly pure powder and were identified by NMR, IR, Fab-Mass analysis. According to NMR spectrum of Figure 1, we confirmed synthesis of TBBPE through proton a ~ e peaks. Each proton peak a, b, c, d, e was located at 7.16, 7.37, 7.42, 7.51, 1.34 ppm, respectively. Proton a and b were more shielded compared to c and d, because a pair of proton a and b is far from ethylene moiety and close to *tert*-butyl group. As a result proton (a-b) and (c-d) pairs showed multiplet skewing effect interacting each other. Also, as the last step reaction proceeded, carbonyl peak of 1650 cm^{-1} in IR completely disappeared in compounds. The resulting products are soluble in common organic solvent such as chloroform and THF.

As shown in Scheme 2, there are two isomers in BPBBPE synthesis according to the coupling direction of reactants. As the last reaction proceeded, the quartets at 7.50, 7.415, 7.335, 7.11, 7.08, 6.97 ppm in NMR were observed due to 50(E):50(Z) isomers.

Figure 2 shows UV-visble and Photoluminescence (PL) spectra of TBBPE and BPBBPE film on glass. The maximum absorbance of BPBBPE and TBBPE appeared at around 344 and 358 nm, which

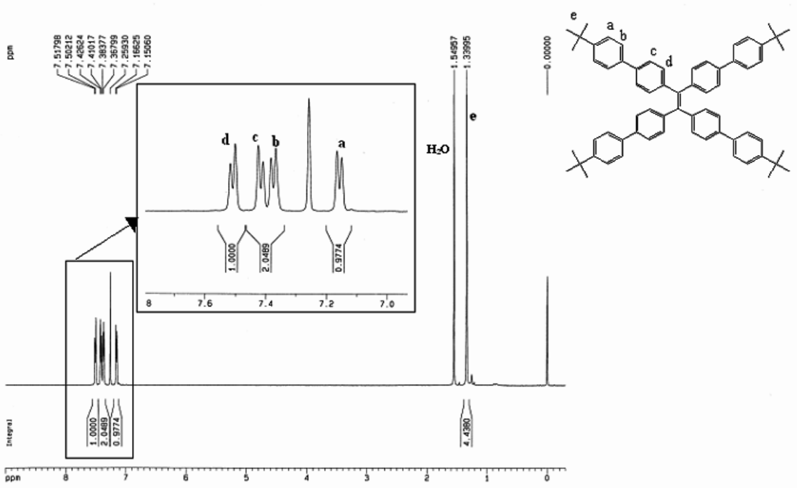


FIGURE 1 ^{1}H-NMR spectrum of TBBPE.

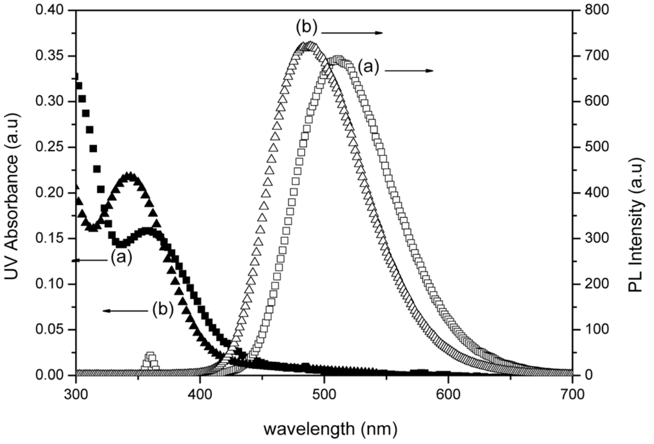


FIGURE 2 UV-visible (Solid) and PL spectra (Open) of TBBPE(a, square) and BPBBPE(b, triangle) film on glass.

are originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bond. Two compounds also showed different PL maximum value as 489 nm (BPBBPE) and 511 nm (TBBPE) due to longer conjugation length of TBBPE. In our previous paper [9], PL maximum wavelength of 1,1,2,2-tetrakis(4′-*tert*-butyl-phenyl)ethene [TBPE] which has been connected phenyl rings with ethylene moiety was found to be 431 nm. TBBPE shows longer conjugation length compared to TBPE due to continuous four phenyl rings. The reason why BPBBPE showed 489 nm PL maximum value was that BPBBPE consisted of half segments of TBPE and TBBPE. Therefore PL maximum value of BPBBPE showed the middle value of TBPE and TBBPE.

The energy band gaps and HOMO, LUMO level of TBBPE and BPBBPE were estimated by cyclic voltammograms (CV) and the analysis of absorption edge with a plot of (hv) vs. $(\alpha hv)^2$, where α, h, and v are absorbance, Plank's constant, and the frequency of light, respectively and summarized in Table 1.

TABLE 1 Electronic Levels of TBBPE, BPBBPE, and Alq_3

	HOMO (eV)	LUMO (eV)	Eg (eV)
TBBPE	5.24	2.24	3.00
BPBBPE	5.22	2.00	3.22
Alq_3	5.80	3.10	2.70

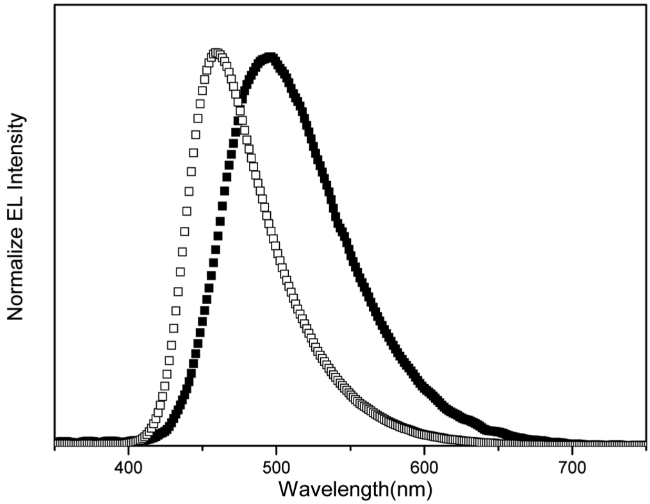


FIGURE 3 EL spectrum of ITO/2-TNATA/TBBPE(solid) or BPBBPE (open)/Alq$_3$/LiF/Al device at 10 mA/cm^2.

EL devices were fabricated in ITO/2-TNATA/TBBPE or BPBBPE/LiF/Al configuration for accurate EL light and ITO/2-TNATA/TBBPE or BPBBPE/Alq$_3$/LiF/Al configuration for increasing EL efficiency. When we compared I-V characteristics of TBBPE and BPBBPE devices, TBBPE device showed slightly better I-V curve than BPBBPE's because there is lower energy barrier between Alq$_3$ and TBBPE's LUMO levels as you see in Table 1.

Figure 3 showed EL maximum value at 496 nm or 469 nm in ITO/2-TNATA(70 nm)/TBBPE (30 nm) or BPBBPE(30 nm)/Alq$_3$(30 nm)/LiF(1 nm)/Al(200 nm) device. The shifted EL maximum value of 15 to 20 nm from PL was observed in devices.

We summarized EL efficiency and CIE values in Tables 2 and 3. TBBPE showed bluish-green CIE values, (0.232, 0.377) and 1.26 cd/A

TABLE 2 Performance Characteristics of Double Layer Device: ITO/2-TNATA (70 nm)/TBBPE or BPBBPE(50 nm)/LiF(1 nm)/Al(200 nm)

	Current density (mA/cm^2)	Voltage (V)	Luminance efficiency (Cd/A)	Power efficiency (Im/W)	C.I.E.
TBBPE	10	16.6	1.26	0.24	(0.232, 0.377)
BPBBPE	10	16.8	0.29	0.05	(0.173, 0.209)

TABLE 3 Performance Characteristics of Triple Layer Device: ITO/2-TNATA (70 nm)/TBBPE or BPBBPE (30 nm)/Alq_3 (30 nm)/LiF(1 nm)/Al (200 nm)

	Current density (mA/cm^2)	Voltage (V)	Luminance efficiency (Cd/A)	Power efficiency (Im/W)	C.I.E.
TBBPE	10	10.0	4.44	1.39	(0.240, 0.435)
BPBBPE	10	10.0	1.87	0.59	(0.177, 0.249)

A at 10 mA/cm^2 in double layer device (ITO/2-TNATA/TBBPE/LiF/Al). BPBBPE also showed blue CIE value, (0.173, 0.209). To increase EL efficiency, we inserted Alq_3 layer between EML and LiF Layer. The related data of triple layer device (ITO/2-TNATA/TBBPE/Alq_3/LiF/Al) are summarized in Table 3. We observed relatively high efficiency of 1.87 cd/A with blue color as (0.177, 0.249) CIE value in BPBBPE emitting system and 4.44 cd/A with (0.240, 0.435) CIE value in TBBPE device. Standard blue efficiency of ITO/2-TNATA(60 nm)/NPB(15 nm)/DPVBi(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al(200 nm) device, which has been commercialized by blue material DPVBi, shows 3.42 cd/A and 1.20 lm/W at 10 mA/cm^2 with (0.168, 0.204) CIE color coordinate value in our device system. When we added Alq_3 layer, we could get better EL efficiency, but could also get green-shifted CIE value because recombination center might be moved from inside of emitter to emitter and Alq_3 interface. Also TBPE which connected four phenyl rings with ethylene moiety showed no EL light and BPBBPE consisted of half segments of TBPE and TBBPE. That is why BPBBPE shows lower EL efficiency than TBBPE device's. Further studies on EL device using these materials and dopant materials are underway.

CONCLUSION

We synthesized blue emitting materials using new chemical structure concept of fully substituted ethylene moieties. The maximum absorbance of BPBBPE and TBBPE appeared at around 344 and 358 nm, which are originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bond. Two compounds also showed different PL maximum value as 489 nm (BPBBPE) and 511 nm (TBBPE) due to longer conjugation length of TBBPE.

EL devices showed EL maximum value at 496 nm or 469 nm in ITO/2-TNATA(70 nm)/TBBPE (30 nm) or BPBBPE(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al(200 nm) device. We observed relatively high efficiency of

1.87 cd/A with blue color as (0.177, 0.249) CIE value in BPBBPE emitting system and 4.44 cd/A with (0.240, 0.435) CIE value in TBBPE device.

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