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Synthesis and Electroluminescent Properties of Fully Substituted Ethylene Moieties

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We synthesized a new bluish-green emitting material using fully substituted ethylene moieties, 1,1,2,2-tetrakis(4′-tert-butyl-phenyl)ethene [TBPE] and 1,1,2,2-tetrakis(4′-tert-butyl-biphenyl)ethene [TBBPE] by McMurry reaction. These products were identified by NMR, IR, Fab-Mass analysis. The maximum absorbance of TBPE and TBBPE appeared at around 318 nm and 358 nm and two compounds also showed different PL maximum value as 431 nm (TBPE) and 511 nm (TBBPE). ITO/2-TNATA/TBBPE/Alq$_3$/LiF/Al device showed bluish-green EL color and 4cd/A efficiency.

Keywords: blue organic light-emitting diode; electroluminescent; McMurry reaction; tetraphenylethylene

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], therefore, numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence (EL), from red, to green, to blue [4–8]. 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 the blue emitting material, the device lifetime and the luminous efficiency, etc.

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In this work we synthesized a new bluish-green emitting material using fully substituted ethylene moieties. Double-layered and triple-layered EL devices were fabricated with synthesized material and evaluated in terms of emission color and luminescence efficiency.

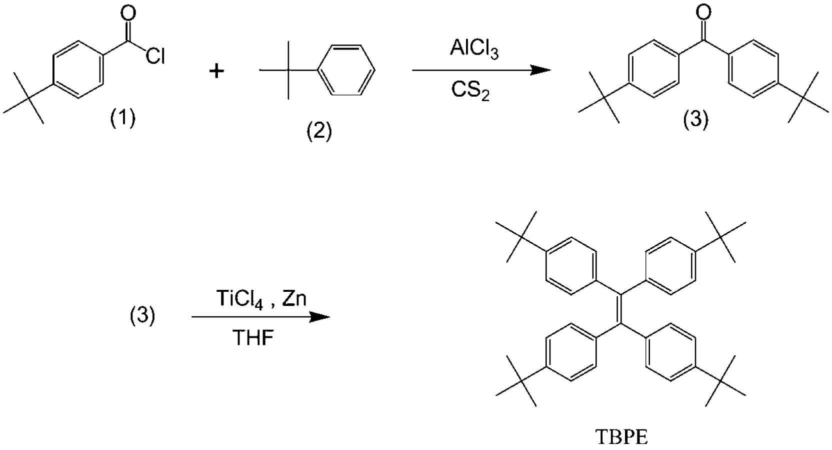
EXPERIMENTAL

Synthesis

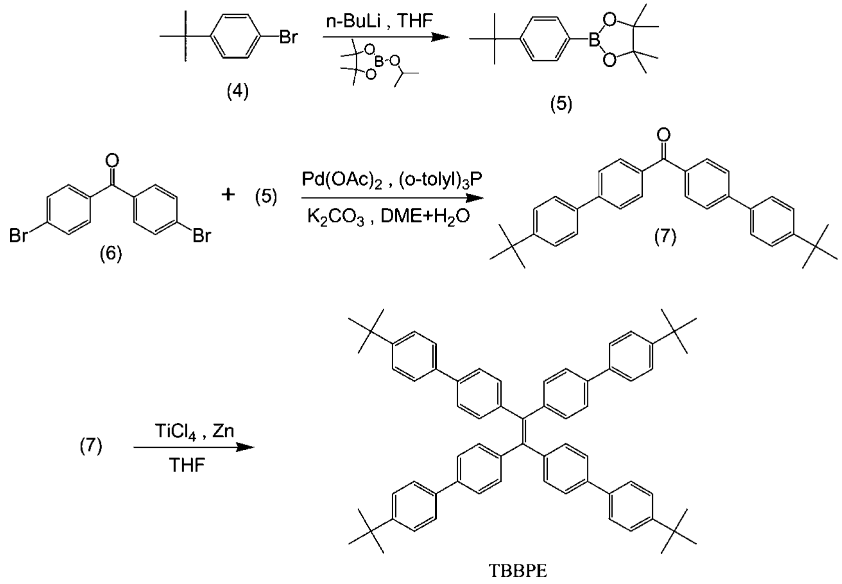
Synthesis of 1,1,2,2-tetrakis(4′-*tert*-butyl-phenyl)ethene [TBPE], 1,1,2,2-tetrakis(4′-*tert*-butyl-biphenyl)ethene [TBBPE]. TBPE and TBBPE in Schemes 1, 2 were obtained by McMurry reaction and the reactants containing ketone moiety were synthesized by Friedel Crafts acylation and Suzuki coupling reaction. Bis(4-*tert*-butylphenyl)methanone (2 g, 6.8 mmol), Zn-powder (1.06 g, 17 mmol) were added to dried THF solvent (150 ml), then $TiCl_4$ (1.5 ml, 13.6 mmol) were added into the reaction mixture. The mixture was heated to 60°C for 1 hr under nitrogen. Reactant mixture was cooling down after 1 hr and then the product was extracted by diethyl-ether. 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. 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 (TBPE) (1.5 g, 79%).

^1H NMR (δ, ppm): 6.93(d, 8H), 7.06(d, 8H), 1.25 (s, 36H).



SCHEME 1 Synthetic route of TBPE.



SCHEME 2 Synthetic route of TBBPE.

TBBPE was obtained by using bis(4′-*tert*-butyl-biphenyl)methanone-(2g, 4.5 mmol) for the McMurry reaction (1.2 g, 63%).

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

Fabrication of OLED

For EL device, TBPE and TBBPE 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. As the last step reaction proceeded, carbonyl peak at around 1645 cm^{-1} in IR was completely disappeared in compounds (Fig. 1).

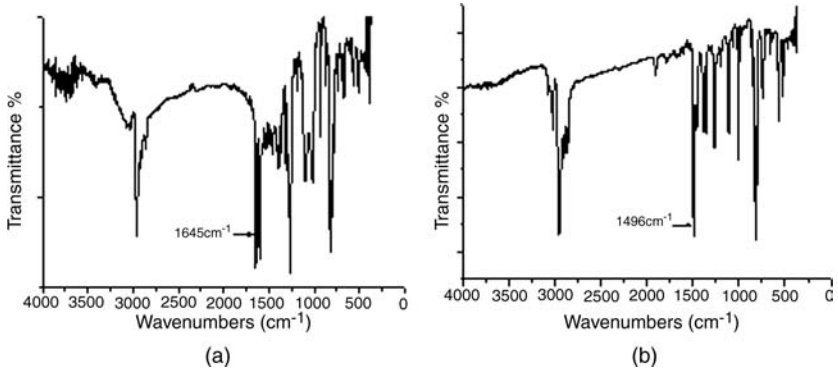


FIGURE 1 IR spectrum of bis(4-*tert*-butylbiphenyl)methanone (a) and TBBPE (b).

Figure 2 shows representative NMR data of TBBPE. At NMR data, we identified proton peaks of TBBPE at around 7.0 ppm and 8.0 ppm. 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 resulting proton (a–b) and (c–d) pairs showed

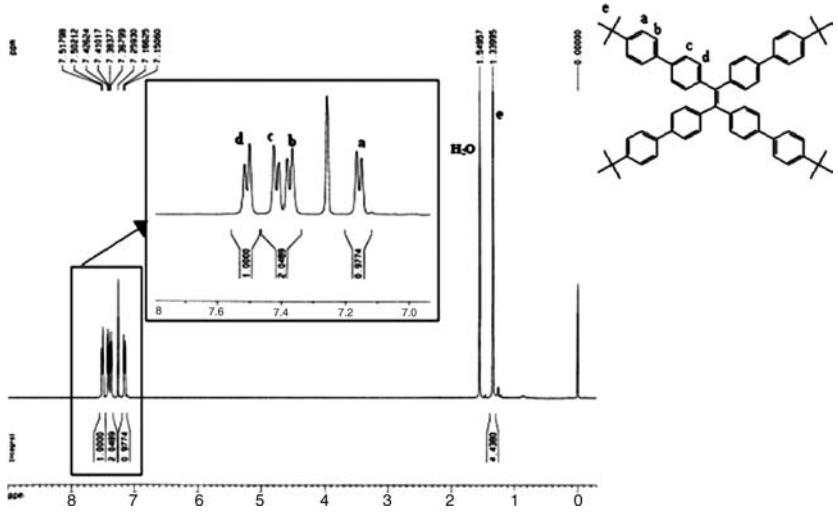


FIGURE 2 NMR spectrum of TBBPE at 500 MHz.

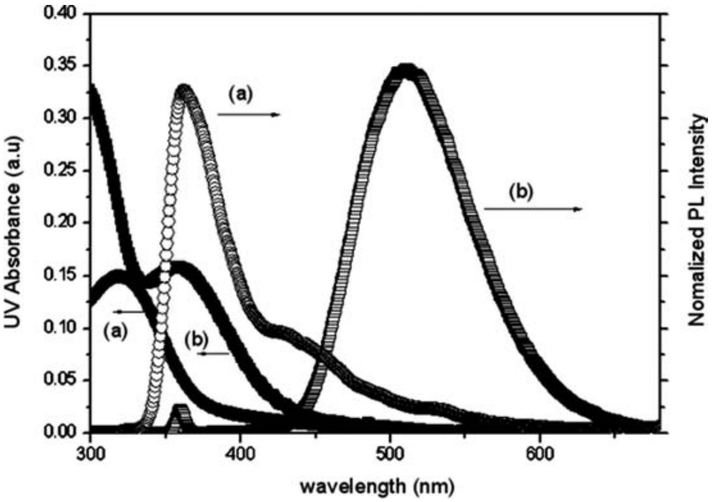


FIGURE 3 UV-visible (solid) and PL spectra (open) of TBPE (a, circle) and TBBPE (b, square) film on glass.

multiplet skewing interacting each other. Fab Mass data of TBBPE was 860. The resulting products are soluble in common organic solvents, such as chloroform and THF.

Figure 3 shows UV-visble and photoluminescence (PL) spectra of TBPE and TBBPE film on glass. The maximum absorbance of TBPE and TBBPE appeared at around 318 nm 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 431 nm (TBPE) and 511 nm (TBBPE) due to longer conjugation length of TBBPE.

The energy band gaps and HOMO, LUMO level of TBPE and TBBPE 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, Planck's constant, and the frequency of light, respectively. Based on these CV results, electro-stability of compounds was achieved. The result accounts that we could get HOMO level value. Electronic levels were summarized in Table 1.

TABLE 1 Electronic Levels of TBPE and TBBPE

	HOMO (eV)	LUMO (eV)	Eg (eV)
TBPE	5.25	1.84	3.41
TBBPE	5.24	2.24	3.00

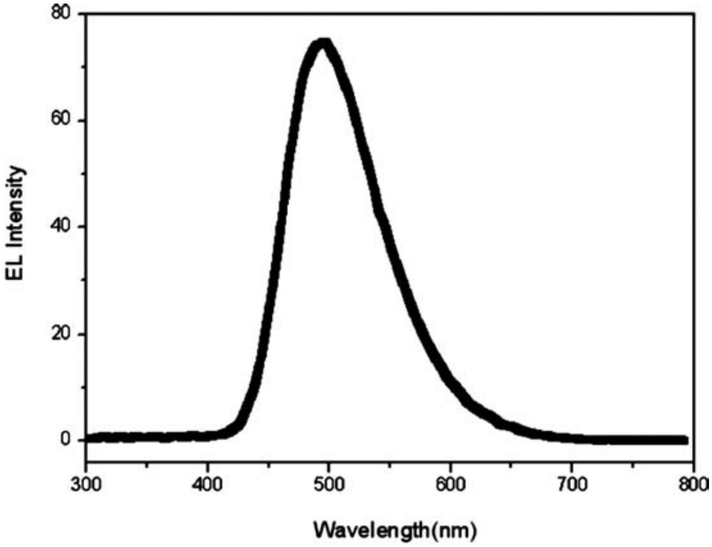


FIGURE 4 EL spectrum of ITO/2-TNATA/TBBPE/Alq3/LiF/Al device at 10 mA/cm^2.

EL devices were fabricated in ITO/2-TNATA/TBPE or TBBPE/Alq$_3$/LiF/Al and ITO/2-TNATA/TBPE or TBBPE/LiF/Al configurations.

Figure 4 showed EL maximum value at 496 nm in ITO/2-TNATA-(70 nm)/TBBPE (30 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (200 nm) device, whereas there is no EL light in TBPE device. It corresponds that PL intensity of TBPE is also about 20 times weaker than TBBPE's. It might be explained by large energy barrier between high LUMO level (1.84 eV) of TBPE and Alq$_3$ LUMO level (3.1 eV). In order to find out original EL maximum wavelength of TBPE and TBBPE, we made EL device without using Alq$_3$ layer. TBPE showed no EL light and TBBPE showed blue EL maximum value of 485 nm. We believe that real EL

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

	Current density (mA/cm^2)	Voltage (V)	Brightness (cd/m^2)	C.I.E	Current efficiency (cd/A)	Power efficiency (Im/w)
TBBPE	10	16.6	126	(0.24, 0.38)	1.26	0.24
	25	18.4	244	(0.24, 0.37)	0.98	0.17

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

	Current density (mA/cm^2)	Voltage (V)	Brightness (cd/m^2)	C.I.E	Current efficiency (cd/A)	Power efficiency (lm/w)
TBBPE	10	10.0	444	(0.24, 0.43)	4.44	1.39
	25	11.8	852	(0.24, 0.43)	3.41	0.91

maximum value of TBBPE is 485 nm. We also suppose that recombination center is near emitter and Alq_3 interface in case of the device containing an Alq_3 layer. It is not clear that there is 26 nm difference between EL and PL maximum values.

We summarized EL efficiency and CIE values in Tables 2 and 3. Table 2 showed bluish-green CIE values, (0.23, 0.38) and 1.26cd/A at 10 mA/cm^2 in double layer device (ITO/2-TNATA/TBBPE/LiF/Al). In Table 3, we observed that the triple layer device (ITO/2-TNATA/TBBPE/Alq_3/LiF/Al) shows relatively higher EL efficiency of 4cd/A, because the carrier charge was normally balanced by Alq_3 ETL layer.

Further studies on these kinds of material derivatives and devices are underway [9].

CONCLUSIONS

We synthesized a new bluish-green emitting material using fully substituted ethylene moieties, 1,1,2,2-tetrakis(4′-*tert*-butyl-phenyl)ethene [TBPE] and 1,1,2,2-tetrakis(4′-*tert*-butyl-biphenyl)ethene [TBBPE] by McMurry reaction. The maximum absorbance of TBPE and TBBPE appeared at around 318 nm 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 431 nm (TBPE) and 511 nm (TBBPE) due to longer conjugation length of TBBPE.

EL devices were fabricated in ITO/2-TNATA/TBPE or TBBPE/Alq_3/LiF/Al and ITO/2-TNATA/TBPE or TBBPE/LiF/Al configurations. TBPE showed no EL light and TBBPE showed blue EL maximum value of 485 nm. We observed that the triple layer device (ITO/2-TNATA/TBBPE/Alq_3/LiF/Al) shows relatively higher EL efficiency of 4cd/A.

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