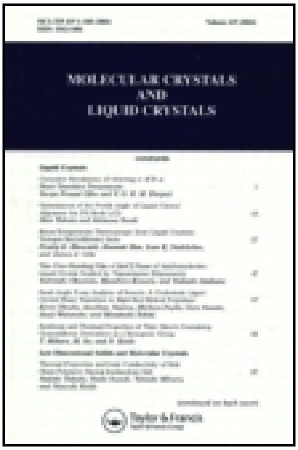

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Electrochemical and Electroluminescent Properties of Fully Substituted Ethylene Moieties

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Electrochemical and Electroluminescent Properties of Fully Substituted Ethylene Moieties

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*We synthesized new blue and bluish green emitting materials using fully substituted ethylene moieties, 1,1,2,2-tetrakis(4-*tert*-butylphenyl)ethene[TBPE], 1,2-di(4′-*tert*-butylphenyl)-1,2-bis(4′-*tert*-butylbiphenyl) ethene [BPBBPE] and 1,1,2,2-tetrakis(4′-*tert*-butylbiphenyl)ethene[TBBPE] by McMurry reaction. EL maximum values of devices are 478 nm and 492 nm in ITO/2-TNATA(60 nm)/NPB(15 nm)/BPBBPE or TBBPE(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al(200 nm) device. TBBPE device showed bluish-green CIE value of (0.236, 0.412) and 5.02cd/A at 10 mA/cm^2. BPBBPE device also showed sky-blue CIE value of (0.218, 0.355) and 2.31cd/A at 10 mA/cm^2.*

Keywords: blue emitting materials; electroluminescent; fully substituted ethylene; McMurry reaction

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]. Although considerable research efforts have been carried out to enhance the performance suitable for practical use, a lot of problems

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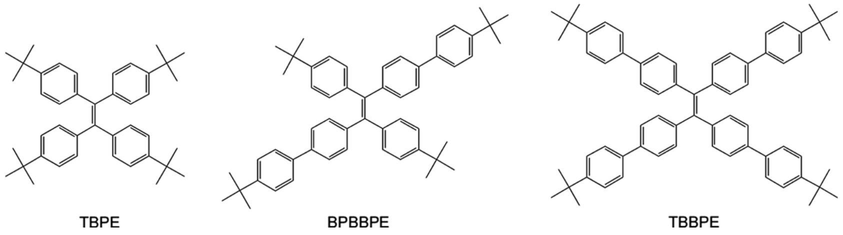

SCHEME 1 Chemical structures of synthesized materials.

to be solved still remain, for example blue emitting material, the device lifetime and the luminous efficiency, etc.

To our knowledge, many attempts have been focused on blue host materials with diarylanthracene, di(styryl)arylene, fluorene and pyrene derivatives [7]. Therefore we propose quite new emitting materials with fully substituted ethylene derivatives, such as 1,1,2,2-tetrakis(4′-*tert*-butylphenyl)ethane [TBPE], 1,2-di(4′-*tert*-butylphenyl)-1,2-bis(4′-*tert*-butyl biphenyl)ethene [BPBBPE] and 1,1,2,2-tetrakis(4′-*tert*-butylbiphenyl)ethane [TBBPE]. We expect that this compound series show high EL efficiency and high thermal property. The Scheme of synthesized materials is shown in Scheme 1.

In our previous article [10], synthesis of TBPE, BPBBPE and TBBPE were reported and discussed. Here, we report the electrochemical property through cyclic voltammetry (CV) method and EL property of multi-layered OLED device including synthesized compounds as well as thermal property.

EXPERIMENTAL

Synthesis

Synthesis of 1,1,2,2-tetrakis(4′-tert-butyl-phenyl)ethene [TBPE], 1,2-di(4′-tert-butyl-phenyl)-1,2-bis(4′-tert-butyl-biphenyl) ethene [BPBBPE], 1,1,2,2-tetrakis(4′-tert-butyl-biphenyl)ethene [TBBPE].

Synthetic procedure of TBPE, BPBBPE and TBBPE was reported in previous paper [10] (see Scheme 1).

[TBPE] ^{1}H NMR δ: 6.93(d, 8H), 7.06(d, 8H), 1.25 (s, 36H).

[BPBBPE] ^{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).

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

Characterization

^{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. Melting point (T_m), grass-transition temperatures (T_g), and crystallization temperatures (T_c) of respective compounds were measured by differential scanning calorimetry (DSC) under nitrogen atmosphere using a DSC2910(TA instrument) and thermogravimetric analysis (TGA) using SDP-TGA2960(TA instrument). 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, enium, FOC) and for reversibility criteria.

For EL device, TBPE, BPBBPE and TBBPE were vacuum-deposited on top of/NPB(150 Å)/2-TNATA (600 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

As shown in Scheme 1, TBPE is the basic structure of tetra-substituted ethylene derivative and ethylene is connected with tertiary butyl phenyl moiety. TBBPE has longer conjugation length than TBPE by using biphenyl group instead of phenyl ring. Biphenyl group has relatively higher fluorescence efficiency of 0.15 [8] than phenyl ring of 0.04 [9]. BPBBPE combined with half segment chromophores of TBPE and TBBPE for comparing chemical structure and luminescence property.

Table 1 shows optical and electrical properties of the synthesized compounds. The maximum absorbance of TBPE, BPBBPE and TBBPE appeared at around 318, 344 and 358 nm, which are originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bond. Three compounds also

TABLE 1 Optical and Electrical Properties of Synthetic Compounds

	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	HOMO (eV)	LUMO (eV)	Eg (eV)
TBPE	364	318	431	5.25	1.84	3.41
BPBBPE	385	344	489	5.22	2.00	3.22
TBBPE	413	358	511	5.24	2.24	3.00

showed different PL maximum values as 413 nm (TBPE), 489 nm (BPBBPE) and 511 nm (TBBPE) because of their different conjugation length. As shown in Scheme 1, TBBPE shows longer conjugation length compared to TBPE and BPBBPE due to continuous four phenyl rings. The reason why BPBBPE showed 489 nm PL maximum value is that BPBBPE consists of half segments of TBPE and TBBPE. Therefore, PL maximum value of BPBBPE showed the middle value of TBPE and TBBPE.

We had checked T_g and T_m by using DSC and TGA experiment in N_2 atmosphere, but there was no obvious T_g and T_m point. On TGA data, we could get T_d point with 280°C of TBPE, 314°C of BPBBPE, and 402°C of TBBPE in 5% loss state which means 95% residue. We believe that T_d point was increased as molecular weight of synthesized three compounds.

To investigate electrochemical kinetic behavior, the measured cyclic voltammograms of TBPE with the various scan rate (30 mV/s ~ 200 mV/s) are shown in Figure 1. The peak potentials are gradually shifted to higher potentials as the scan rate was increased.

The redox current value gradually increased as the scan rate increased. This result suggest that the electrochemical process of TBPE is reproducible in the potential range of $-1 \sim 1\,V$ vs. Ag/Ag^+.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [11]:

$$i_{p,a} = k\ v^x \tag{1}$$

$$\log i_{p,a} = \log k + x \log v \tag{2}$$

where $i_{p,a}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Assuming that electrode kinetics satisfies Eq. (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where $x = 1$, or the reactant diffusion process, where $x = 0.5$ [11].

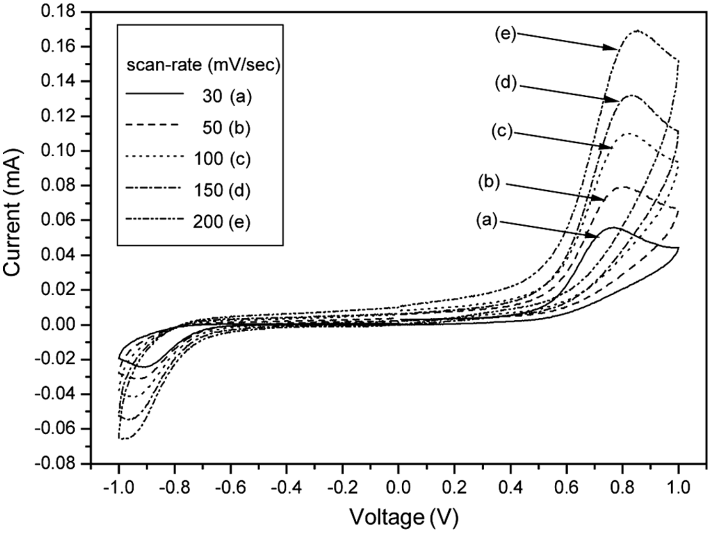

FIGURE 1 Cyclic voltammograms of TBPE with various scan rate (0.1 M $(n\text{-}Bu)_4NBF_4$/DMF). (a) 200 mV/sec, (b) 150 mV/sec, (c) 100 mV/sec, (d) 50 mV/sec, sec, (e) 30 mV/sec.

The oxidation current density of TBPE versus the scan rate is approximately linear relationship in the range of 30 ~ 200 mV/sec. The exponent of scan rate, x, value of TBPE is found to be 0.55. Also, CV results of BPBBPE and TBBPE showed similar shapes and x values with TBPE's (x of BPBBPE = 0.51, x of TBBPE = 0.48).

The band gap energies of TBPE, BPBBPE and TBBPE are estimated to be 3.41, 3.22 and 3.00 eV, respectively. Base on onset point of UV-visible spectrum and CV data, we calculated HOMO and LUMO levels. The energy band gaps, HOMO, LUMO level, UV_{onset}, UV and PL maximum were summarized in Table 1.

EL devices were fabricated in ITO/2-TNATA(60 nm)/NPB(15 nm)/TBPE or BPBBPE or TBBPE(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al(200 nm) device configuration.

When we compared I–V characteristics of BPBBPE and TBBPE devices (Fig. 2), TBBPE device showed better I–V curve than BPBBPE's because there is lower energy barrier between Alq_3 and TBBPE's LUMO levels. Also, there is no normal EL light in TBPE device and it corresponds that PL intensity of TBPE is also about 20 times weaker than TBBPE's. In addition to, 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) (Table 1).

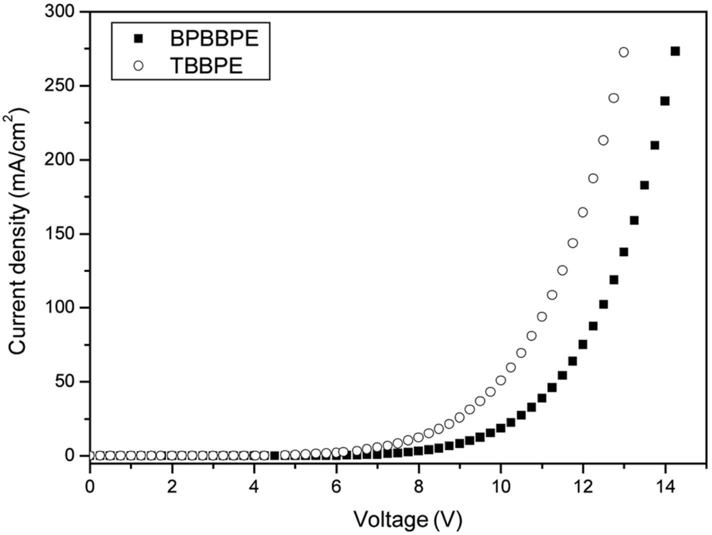

FIGURE 2 Current density-voltage characteristics of ITO/2-TNATA(60 nm)/NPB(15 nm)/BPBBPE(■) or TBBPE(○)(30 nm)/Alq$_3$(30 nm)/LiF(1 nm)/Al device.

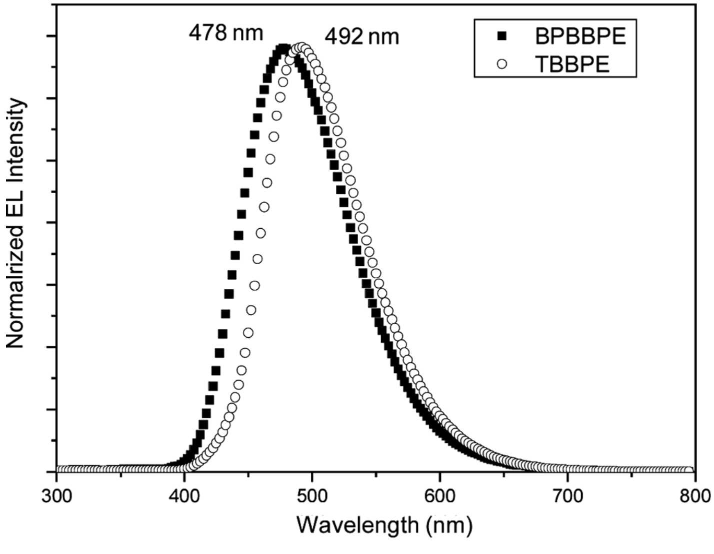

FIGURE 3 EL spectrum of ITO/2-TNATA(60 nm)/NPB(15 nm)/BPBBPE(■) or TBBPE(○)(30 nm)/Alq$_3$(30 nm)/LiF(1 nm)/Al device at 10 mA/cm^2.

TABLE 2 Electroluminescent Property of Multi-Layered Device: ITO/2-TNATA(60 nm)/NPB(15 nm)/BPBBPE or TBBPE(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al (200 nm) device at 10 mA/cm^2

	EL_{max} (nm)	Voltage (V) (@10 mA/cm^2)	Luminance efficiency (cd/A)	Power efficiency (lm/W)	C. I. E. (x, y)
BPBBPE	478	9.0	2.31	0.81	0.218, 0.335
TBBPE	492	8.9	5.02	1.78	0.236, 0.412

Figure 3 showed EL maximum value at 478 nm or 492 nm in ITO/2-TNATA(60 nm)/NPB(15 nm)/BPBBPE or TBBPE (30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al(200 nm) device. The shifted EL maximum value of 10 to 20 nm from PL was observed in devices, but the explanation of shifted EL maximum value is not clear.

We summarized EL efficiency and CIE values in Table 2. TBBPE showed bluish-green CIE value of (0.236, 0.412) and 5.02cd/A at 10 mA/cm^2. BPBBPE also showed sky-blue CIE value of (0.218, 0.355) and 2.31 cd/A at 10 mA/cm^2. TBPE which connected four phenyl rings with ethylene moiety showed no EL light and BPBBPE consists of half segments of TBPE and TBBPE. That is why BPBBPE shows about half EL efficiency of TBBPE device's.

Further studies on EL device using these materials and dopant materials are underway.

CONCLUSIONS

The maximum absorbance of TBPE, BPBBPE and TBBPE appeared at around 318, 344 and 358 nm, which are originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bond. Three compounds also showed different PL maximum values as 413 nm (TBPE), 489 nm (BPBBPE) and 511 nm (TBBPE) because of their different conjugation length. The oxidation current density of TBPE versus the scan rate is approximately linear relationship in the range of $30 \sim 200$ mV/sec. The exponent of scan rate, x, value of TBPE is found to be 0.55. Also, CV results of BPBBPE and TBBPE showed similar shapes and x values with TBPE's (x of BPBBPE = 0.51, x of TBBPE = 0.48). TBBPE showed bluish-green CIE value of (0.236, 0.412) and 5.02 cd/A at 10 mA/cm^2. BPBBPE also showed sky-blue CIE value of (0.218, 0.355) and 2.31cd/A at 10 mA/cm^2.

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