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We synthesized new bluish-green and sky-blue emitting materials, 1,1,2,2-tetrakis(4'-tert-butylbiphenyl)ethane[TBBPE] and 1,1,2,2-tetrakis(4-(anthracen-9yl)phenyl)ethene[TAPE]. TBBPE and TAPE film showed PL maximum value of 511 nm and 492 nm. TBBPE OLED device showed bluish-green C.I.E. value of (0.236, 0.412) and high luminance efficiency of 5.02 cd/A at 10 mA/cm^2 . TAPE device also showed sky-blue C.I.E. value of (0.213, 0.323) and 3.17 cd/A at 10 mA/cm^2 . It is found that TBBPE shows better luminance efficiency than TAPE and TAPE device exhibits relatively lower operating voltage and better C.I.E. value than TBBPE device.

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], numerous conjugated organic molecules have been synthesized and reported

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to exhibit electroluminescence (EL), from red, to green, to blue [4–6]. In order to make full color OLED display, we need high performance red, green, blue materials with high EL efficiency, pure color coordinate (C.I.E.) value and long life time as well as material thermal property. Host and dopant method in fluorescence and phosphorescence system have been used to get high efficiency of OLED and red and green emitters have been developed and improved to commercialize full color OLED. However, a lot of problems to solve still remain, for example blue emitting material, the device lifetime and the luminous efficiency, etc.

Many kinds of blue materials including diarylanthracene, di(styryl) arylene, fluorene and pyrene have been intensively used and studied on improved EL property [6]. Conventional one of the commercialized compounds is 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl(DPVBi) of Idemitsu kosan, but DPVBi has low Tg of 64° C [7,8]. And it causes recrystallization under long operation and relatively short device life time compared to green and red color.

In our work, we tried to synthesize new blue chemical structure including tetra substituted ethylene and anthracene moieties. Chemical structure of tetra substituted ethylene means fully substituted chromophore in a molecule and it can provide highly thermal property due to increased molecular weight compared to not fully substituted compound such as stilbene moiety.

In this study, we synthesized new tetra substituted ethylene derivatives including benzene and anthracene moieties and characterized their own electrical and optical properties. The resulting material, 1,1,2,2-tetrakis(4'-tert-butylbiphenyl)ethene[TBBPE] and 1,1,2,2-tetrakis(4-(anthracen-9-yl)phenyl)ethene[TAPE] were synthesized through Suzuki and McMurry reaction. Electro-optical properties of these materials were characterized by cyclic voltammetry (CV), UV-visible and photoluminescence (PL) spectra. Moreover, multilayer EL devices were fabricated using these materials as non-doped emitting layer.

EXPERIMENTAL

Synthesis

Synthesis of 1,1,2,2-tetrakis(4'-tert-butylbiphenyl) Ethene [TBBPE]

i) 2-(4-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(1). 1-tert-Butyl-4-bromobenzene(5 ml, 28.7 mmol) was dissolved in 200 ml of dry THF solution and stirred at -78° C, then 1.6 M n-BuLi 35 ml was added. And then isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(11 ml, 57.5 mmol) was added to the reaction after 30 min. After the reaction finished, the reaction mixture was extracted with diethyl-ether and water. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in acetone and added to methanol. The precipitate was filtered and washed with methanol (7 g, 93.8%).

¹H NMR (δ , ppm): 7.69(d, 2H), 7.43(d, 2H), 1.32(d, 21H); Fab⁺-mass: 260

ii) Bis(4'-tert-butylbiphenyl)methanone(2). Bis(4-bromophenyl)methanone(2 g, 5.7 mmol), 2-(4-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(1) (3.26 g, 12.5 mmol), Pd(OAc)₂ (0.64 g, 2.85 mmol), (tris-o-tolyl)₃P (0.86 g, 2.85 mmol) were added to DME (250 ml) solution, then the prepared K₂CO₃ solution, which was dissolved in DME and H₂O (1:1, 100 ml) solvent, was added to reaction mixture. After the reaction finished, the reaction mixture was extracted with diethyl-ether and water. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol (2 g, 76%).

¹H NMR (δ , ppm): 7.92(d, 4H), 7.72(d, 4H), 7.62(d, 4H), 7.52(d, 4H), 1.38(s, 18H); Fab⁺-mass: 446.

iii) 1,1,2,2-tetrakis(4'-tert-butylbiphenyl)ethene [TBBPE]. Bis(4'-tertbutylbiphenyl)methanone(2) (2 g, 4.5 mmol), Zn-powder (1.06 g, 17 mmol) were added to dried THF solvent (150 ml), then TiCl₄(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 MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol. Yellowish powder was purified by column chromatography with CHCl₃: n-hexane (1:1) eluent to afford beige solid (TBBPE) (1.2 g, 63%).

¹H NMR (δ, ppm): 7.16(d, 8H), 7.37(d, 8H), 7.42(d, 8H), 7.51(d, 8H), 1.34 (s, 36H); Fab⁺-mass: 860.

Synthesis of 1,1,2,2-tetrakis(4-(Anthracen-9-yl)Phenyl)Ethene [TAPE]

i) Anthracen-9-yl-9-boronic acid(3). 9-bromoanthracene (4g, 15.3 mmol) was dissolved in 200 ml of dry THF solution and stirred at -78° C, then 1.6 M n-BuLi 20 ml was added. And then triethyl borate (5.3 ml, 3.1 mmol) was added to the reaction after 30 min. After the reaction finished, it was then acidified with 2 N HCl solution, and

extracted with diethyl-ether and water. The organic layer was dried by anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was dissolved in acetone and added to CCl_4 . The precipitate was filtered and washed with CCl_4 . (2.5 g, 72.1%).

 ^{1}H NMR (δ , ppm): 8.47(s, 1H), 8.12(d, 2H), 8.01(d, 2H), 7.48(m, 4H), 5.07 (s, 2H); Fab $^{+}$ -mass: 222.

ii) Bis(4-(anthracen-9-yl)phenyl)methanone(4). Bis(4-bromophenyl) methanone (1.7 g, 5 mmol), Anthracen-9-yl-9-boronic acid(3)(2.5 g, 11.2 mmol), Pd(PPh₃)₄ (0.23 g, 0.2 mmol) were added to Toluene (250 ml) solution, then the prepared K₂CO₃ solution, which was dissolved in H₂O solvent, was added to reaction mixture. After the reaction finished, the reaction mixture was extracted with diethyl-ether and water. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol (2 g, 74.9%).

¹H NMR (δ ,ppm): 8.54(s, 2H), 8.20(d, 4H), 8.07(d, 4H), 7.70(d, 4H), 7.65(d, 4H), 7.49(t, 4H), 7.40 (t, 4H); Fab⁺-mass: 534.

iii) 1,1,2,2-tetrakis(4-(anthracen-9-yl)phenyl)ethene [TAPE]. Bis(4-(anthracen-9-yl)phenyl)methanone(4) (2g, 3.74 mmol), Zn-powder (0.88 g, 14.1 mmol) were added to dried THF solvent (150 ml), then TiCl₄ (1.25 ml, 11.3 mmol) were added into the reaction mixture. The mixture was heated to 60° C for 1hr under nitrogen. Reactant mixture was cooling down after 1hr and then the product was extracted by diethyl-ether. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol.

Yellow powder was purified by column chromatography with $CHCl_3$: n-hexane (1:1) eluent to afford greenish-yellow solid (TAPE) (1.1 g, 56.7%).

 ^{1}H NMR (δ , ppm): 8.50(s, 4H), 8.03(d, 8H), 7.74(d, 8H), 7.67(d, 8H), 7.43(d, 8H), 7.35(t, 8H), 7.08 (t, 8H); Fab $^{+}$ -mass: 1037.

Characterization

¹H 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 ~ 200 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/AgNO₃ referenced electrode. Ferrocene was used for potential calibration (all reported potentials are referenced against ferrocene/ferrocenium, FOC) and for reversibility criteria.

For EL device, TBBPE and TAPE 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 1Å/sec to give an emitting area of 4 mm² 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

The synthesized compounds were prepared by >75% yield of Suzuki reaction and >50% yield of McMurry reaction (Schemes 1 and 2). These products were finally purified with column method to have highly pure powder and were identified NMR, Fab⁺-mass.



SCHEME 1 Synthetic route of TBBPE.



SCHEME 2 Synthetic route of TAPE.

Figure 1 shows UV-visible and PL spectra of TBBPE and TAPE films deposited on glass. TAPE exhibited typical anthracene UV absorption peak of 355 nm, 375 nm and 395 nm. Although two compounds show similar onset point values of 413 and 414 nm in UVvisible spectra, PL maximum values of TBBPE and TAPE are 511 and 492 nm. We suppose that there is twisted angle between anthracene and phenyl ring. Sakata *et al.* has also reported that 9-phenylanthracene gives 90 degree of twisted angle in previous paper [9]. It means that twisted anthracene group in TAPE compound may cause



FIGURE 1 UV-visible (solid) and PL spectra (open) of $\text{TBBPE}(\blacksquare)$ and $\text{TAPE}(\bigcirc)$ film on glass.

to make decreased conjugation length and longer intermolecule distance.

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 high T_d point with 402°C of TBBPE and 368°C of TAPE in 5% loss state which means 95% residue.

The bang gap energy of TBBPE and TAPE are estimated to be 3.00, 2.99 eV respectively. Based 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 values were summarized in Table 1.

As shown in Table 1, TAPE has lower HOMO level of 5.61 eV compared to TBBPE's. This might be due to anthracene moiety which has stable electrochemical oxidation characteristics. In conventional anthracene derivatives, 9,10-di-(2-naphthyl)anthracene(ADN) and 2-methyl-9,10-di-(2-napthyl)anthracene(MADN) show same HOMO level of 5.5 eV because of anthracene moiety [6].

EL devices were fabricated using 4,4',4"-tris{N,-(2-naphthyl)-N-phenylamino}-triphenylamine (2-TNATA) as a hole injection layer (HIL), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB) as a hole transporting layer (HTL), TBBPE and TAPE as emitting layer (EML), tris-(8-hydroxyquinolate)-aluminum(Alq₃) as electron transporting layer (ETL), ITO as the anode and LiF/Al as the cathode; ITO/2-TNATA (60 nm)/NPB (15 nm)/TBBPE or TAPE(30 nm)/Alq₃(30 nm)/LiF (1 nm)/Al (200 nm).

When we compared I-V characteristics of TBBPE and TAPE devices (Fig. 2), TAPE device showed better I-V curve than TBBPE's. The reason could be explained by that the LUMO energy level difference between TBBPE and Alq_3 is larger value of 0.86 eV than 0.48 eV of TAPE case.

Figure 3 showed EL maximum values of 492 nm and 474 nm in ITO/2-TNATA(60 nm)/NPB(15 nm)/TBBPE or TAPE(30 nm)/Alq₃(30 nm)/LiF(1 nm)/Al(200 nm) device. The shifted EL maximum value of about 20 nm from PL was observed in devices, but the explanation of shifted EL maximum value is not clear. According to EL

| | $UV_{onset} \\ (nm)$ | UV _{max} (nm) | PL _{max} (nm) | HOMO (eV) | LUMO (eV) | Eg (eV) |
|---------------|---|--|---------------------------|----------------|----------------|----------------|
| TBBPE TAPE | $\begin{array}{c} 413\\ 414\end{array}$ | $\begin{array}{c} 358\\ 395 \end{array}$ | $511 \\ 492$ | $5.24 \\ 5.61$ | $2.24 \\ 2.62$ | $3.00 \\ 2.99$ |

TABLE 1 Optical and Electrical Properties of Synthetic Compounds



FIGURE 2 Current density-voltage characteristics of ITO/2-TNATA(60 nm)/ NPB(15 nm)/TBBPE(\blacksquare) or TAPE(\bigcirc)(30 nm)/Alq₃(30 nm)/LiF(1 nm)/Al device (inset: energy diagram).



FIGURE 3 EL Spectrum of ITO/2-TNATA(60 nm)/NPB(15 nm)/TBBPE(\blacksquare) or TAPE(\bigcirc)(30 nm)/Alq₃(30 nm)/LiF(1 nm)/Al device at 10 mA/cm².

| | EL _{max} (nm) | Voltage (V) | Luminance efficiency (cd/A) | Power efficiency (lm/W) | C. I. E. (x, y) |
|---------------|---------------------------|----------------|-----------------------------------|---|------------------------------|
| TBBPE TAPE | 492 474 | 8.9 6.8 | $5.02 \\ 3.17$ | $\begin{array}{c} 1.78\\ 1.46\end{array}$ | 0.236, 0.412 0.213, 0.323 |

 $\begin{array}{l} \textbf{TABLE 2} \hspace{0.1cm} \text{Electroluminescent Property of Multi-Layered Device: ITO/} \\ \text{2-TNATA(60 nm)/NPB(15 nm)/TBBPE or TAPE(30 nm)/Alq_3(30 nm)/} \\ \text{LiF}(1 nm)/Al(200 nm) \hspace{0.1cm} \text{device at } 10 \hspace{0.1cm} \text{mA/cm}^2 \end{array}$

device, TAPE also showed blue shifted maximum wavelength of 18 nm from TBBPE's and this tendency is similar with PL result.

We summarized EL efficiency and C.I.E. values in Table 2. TBBPE OLED device showed bluish-green C.I.E. value of (0.236, 0.412) and high luminance efficiency of 5.02 cd/A at 10 mA/cm^2 . TAPE device also showed sky-blue C.I.E. value of (0.213, 0.323) and 3.17 cd/A at 10 mA/cm^2 . It is found that TBBPE shows better luminance efficiency than TAPE and TAPE device exhibits relatively lower operating voltage and better C.I.E. value than TBBPE device. The reason of blue shifted EL maximum value in TAPE device may be that anthracene moiety causes twisted intramolecule angle and decreased conjugation length. As we discussed earlier, 9-phenylanthracene group includes 90 degree twisted angle [9] and it breaks molecular planarity and decreases conjugation length. Moreover, we believe that bulkiness of anthracene group increases intermolecular distance and this prevents molecular stacking which is related with longer emission wavelength.

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

CONCLUSIONS

We synthesized new bluish-green and sky-blue emitting materials, 1,1,2,2-tetrakis(4'-tert-butylbiphenyl)ethane[TBBPE] and 1,1,2,2-tetrakis(4-(anthracen-9-yl)phenyl)ethene[TAPE].

TAPE exhibited typical anthracene UV absorption peak of 355 nm, 375 nm and 395 nm. Although two compounds show similar onset point values of 413 and 414 nm in UV-visible spectra, PL maximum values of TBBPE and TAPE are 511 and 492 nm. It means that there is twisted angle between anthracene and phenyl ring. We believe that twisted anthracene group in TAPE compound may cause to make decreased conjugation length and longer intermolecule distance. TBBPE OLED device showed bluish-green C.I.E. value of (0.236, 0.412) and high luminance efficiency of 5.02 cd/A at 10 mA/cm^2 . TAPE device also showed sky-blue C.I.E. value of (0.213, 0.323) and 3.17 cd/A at 10 mA/cm^2 . It is found that TBBPE shows better luminance efficiency than TAPE and TAPE device exhibits relatively lower operating voltage and better C.I.E. value than TBBPE device. The reason of blue shifted EL maximum value in TAPE device may be that anthracene moiety causes twisted intramolecule angle and decreased conjugation length.

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