

Fully Substituted Ethylene as a New Class of Highly Efficient Blue Emitting Materials for OLEDs

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Abstract

We synthesized new blue and bluish green emitting materials by using fully substituted ethylene moieties. Multi-layered EL devices were fabricated with synthesized materials and evaluated in terms of emission color and luminescence efficiency.

BPBAPE[EML 4] having high T_g of 155 °C showed luminance and power efficiency of 10.33cd/A and 4.0 lm/W without any doping agent. BTBPPA[EML 5] exhibited 5cd/A and 1.67lm/W efficiency with blue CIE value of (0.165, 0.195).

1. Introduction

Organic light-emitting diodes (OLEDs) based on organic molecules are currently a major subject of an intense research effort due to their promise to the manifestation of full-color large display applications [1-3]. Numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence (EL), from red to green and blue [4-10]. Although considerable research efforts in Organic light-emitting diodes (OLEDs) field have been carried out to enhance the performance suitable for practical use, a lot of problems have still remained. For example, blue color materials applied to color mobile phone market and took growing public interests but display panel manufacturer still cannot satisfied with the current blue performance as a high performance color display panel. And highly efficient blue emitting materials are the subjects to be solved.

In this work we synthesized new blue and bluish green emitting materials by using fully substituted ethylene moieties. Multi-layered EL

devices were fabricated without any doping agent and evaluated in terms of emission color and luminescence efficiency.

2. Experimental

2.1. General Methods

^1H NMR spectra were recorded on a Bruker, Advance DPX-300 and Advance 500. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series 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 100mV/s. The compound was dissolved in N,N-Dimethylformamide (DMF) with 0.1M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated Ag/AgNO₃ reference electrode. Ferrocene was used for potential calibration.

For EL device, EML1 ~ EML5 were vacuum-deposited on top of NPB(15 Å)/2-TNATA (600 Å)/ITO(1200 Å/30ohm) under 10⁻⁶ torr, the rate of deposition being 1 Å/sec to give an emitting area of 4mm² and other organic layer and aluminum layer were continuously deposited under the same vacuum condition. Current-voltage (I-V) characteristics of the fabricated OLEDs were measured by using Keithley 2400 electrometer. Light intensity was obtained by

Minolta CS-1000.

2.2. Synthesis

1,1,2,2-tetrakis(4'-tert-butyl-phenyl)ethene [TBPE, EML 1], 1,1,2,2-tetrakis(4'-tert-butyl-biphenyl) ethene [TBBPE, EML 2] and 1,2-di(4'-tert-butyl-phenyl)-1,2-bis(4'-tert-butyl-biphenyl)ethane [BPBBPE, EML 3].

EML 1, EML 2 and EML 3 in scheme I were obtained by McMurry reaction and the reactants containing ketone moiety which were synthesized by Friedel Crafts acylation and Suzuki coupling reaction. Bis(4-tert-butylphenyl)methanone(2g, 6.8mmol), Zn-powder (1.06g, 17mmol) was added to dried THF solvent(150ml), and then TiCl₄(1.5ml,13.6mmol) were added into the reaction mixture. The mixture was heated to 60 °C for an hour under nitrogen. After the reaction mixture cooled, and extracted with diethyl-ether. The organic layer dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol.

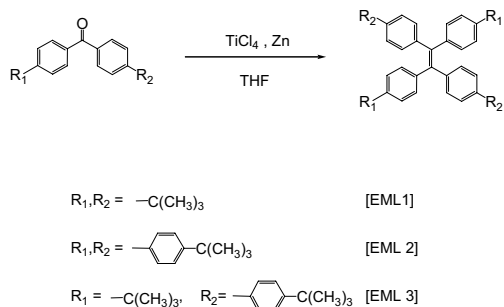
Yellowish powder was purified by column chromatography with CHCl₃ : n-hexane (1:1) eluent to afford white solid(EML 1) (1.5g, 79%)
¹H NMR : δ: 6.93(d, 8H), 7.06(d, 8H), 1.25 (s, 36H)

EML 2 was obtained by using Bis(4'-tert-butylbiphenyl)methanone(2g,4.5mmol) for the McMurry reaction. (1.2g, 63%)
¹H NMR : δ: 7.16(d, 8H), 7.37(d, 8H), 7.42(d, 8H), 7.51(d, 8H), 1.34 (s, 36H)

EML 3 was obtained by using (4-tert-butylphenyl)(4'-tert-butylbiphenyl) methanone(2g, 5.4mmol) as McMurry reaction. (1.2g, 63%)

¹H 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)

Structure and synthesis method of BPBAPE[EML 4] and BTBPPA[EML 5] will be reported later.



Scheme 1. Last synthesis step of EML 1, EML 2 and EML 3

3. Result 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 in scheme 1, carbonyl peak at around 1645cm⁻¹ in IR was completely disappeared in compounds.

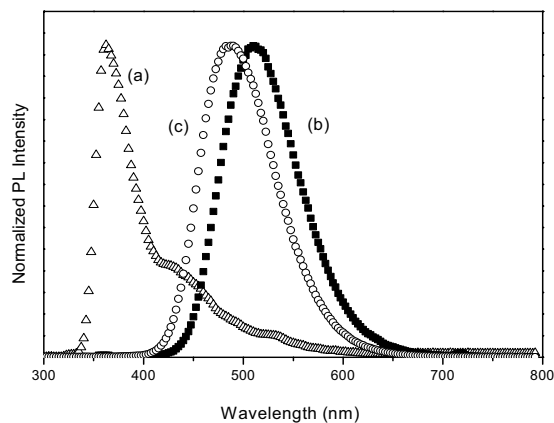


Figure 1. PL spectra of EML 1 (Δ , a), EML 2 (\blacksquare , b) and EML 3 (\circ , c)

Figure.1 shows photoluminescence (PL) spectra of EML 1, EML 2 and EML 3 in the film state on glass. The maximum absorbance of EML 1, EML 2 and EML 3 appeared at around 318nm, 358nm and 344nm (Table 1) which were originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bonds. Three compounds also showed different PL maximum value as 431nm (EML 1), 511nm (EML 2) and 489nm (EML 3). The longest wavelength of EML 2 can be

analyzed by the longer conjugation length of EML 2.

EML 4 and 5 showed PL maximum values of 489nm and 463nm respectively as shown in figure 2.

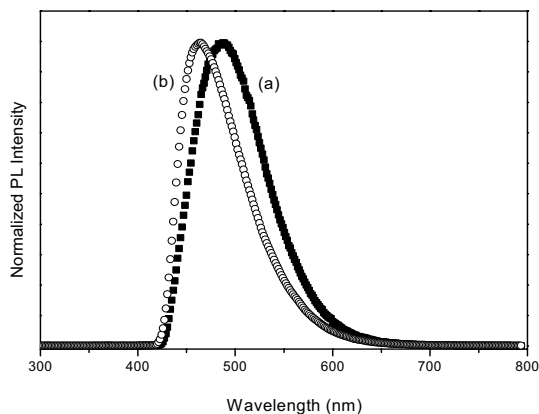


Figure 2. PL spectra of EML 4 (■, a) and EML 5 (○, b)

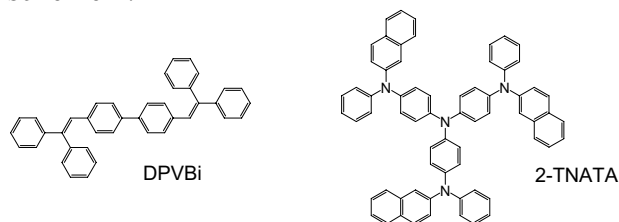
The energy band gaps and HOMO, LUMO levels of EML 1~5 were estimated by cyclic voltammograms(CV) and the analysis of absorption edge with a plot of (hv) vs. $(ahv)^2$, where a , h , and v are absorbance, Plank's constant, and the frequency of light, respectively. Based on CV results, electrochemical stability of compounds was confirmed. The CV result accounts for that we could get HOMO level value. Electronic levels were summarized in Table 1.

	UV (nm)	PL (nm)	HOMO (eV)	LUMO (eV)	Eg (eV)
EML 1	318	431	5.25	1.84	3.41
EML 2	358	511	5.24	2.24	3.00
EML 3	344	489	5.22	2.00	3.22
EML 4	392	489	5.45	2.42	3.03
EML 5	400	463	5.31	2.36	2.95

Table 1. Absorption, emission spectra maxima and energy values of EML 1 ~ 5

EL devices were fabricated in ITO/ 2-TNATA (60nm)/ NPB(15nm)/ EML 1 ~ 5 (30nm)/ Alq₃ (30nm)/ LiF (1nm)/ Al(200nm) device configuration for EL properties. For comparison with the standard device, we used

4,4'-bis-(2,2-diphenyl-vinyl)-biphenyl (DPVBi) as an emitting material, N,N'-di(naphthalene-1-ly)-N,N'-diphenyl-benzidine (NPB) as a hole transporting material and 4,4',4''-tris(N-(2-naphthyl)-N-phenyl-amino)-triphenylamine(2-TNATA) as a hole injection material as shown in scheme 2.



Scheme 2. DPVBi and 2-TNATA

Figure 3. showed I-V characteristics of these devices. EML 4 exhibited the best I-V performance in this series including DPVBi emitting material, because EML 4 has the proper electronic level matched with NPB and Alq₃.

EML 1 showed no EL light in the device. It might be explained by the large energy barrier between high LUMO level (1.84eV) of EML 1 and Alq₃(3.1eV) and chromophore intrinsic property. It corresponds with that PL intensity of EML 1 is also about 20 times weaker than EML 2 and 3's.

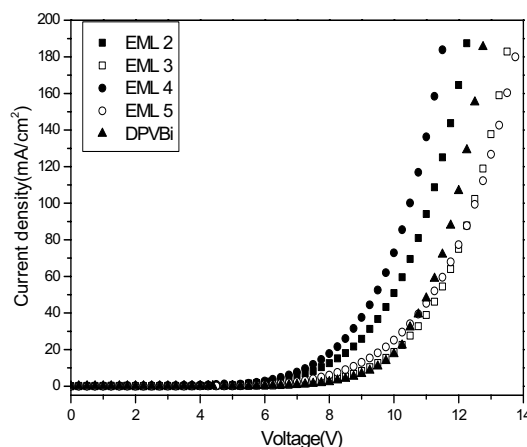


Figure 3. I-V characteristics for ITO/ 2-TNATA (60nm)/ NPB(15nm)/ EML 2 (■) or EML 3(□) or EML 4(●) or EML 5(○) or DPVBi(▲) (30nm)/ Alq₃ (30nm)/ LiF(1nm)/ Al(200nm) device.

EL maximum values of EML 2~5 showed at 497nm, 478nm, 475nm and 463nm respectively as shown in figure 4, which were blue-shifted from PL maximum values. EL maximum value tendency in these series corresponds with PL's.

PL and EL maximum values of EML 3 were in the middle between EML 1 and 2, which could be explained by that EML 3 consisted with half segments of EML 1 and 2 chromophore.

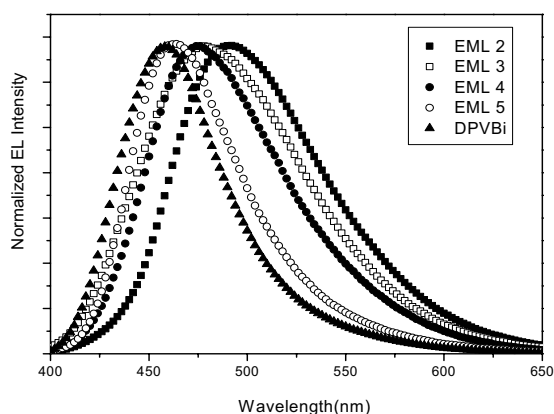


Figure 4. EL spectra of ITO/ 2-TNATA (60nm)/ NPB(15nm)/ EML 2 (■) or EML 3(□) or EML 4(●) or EML 5(○) or DPVBi(▲) (30nm)/ Alq₃ (30nm)/ LiF(1nm)/ Al(200nm) device.

We summarized EL performance in table 2. EML 2 showed 5cd/A luminance efficiency with bluish-green color of (0.236, 0.412) and EML 3 exhibited lower EL efficiency and better CIE value than EML 2's. It might be due to the mixed chemical structure of EML 1 and 2.

In order to increase EL performance, we inserted other chromophore moiety into an ethylene moiety and balanced the angle of intrachemical structure in EML 4 and 5.

EML 4 showed much better luminance and power efficiency of 10.33 cd/A and 4.0 lm/W without doping system although it had worse CIE value than DPVBi's as shown in table 2. EML 5 also exhibited better luminance and power efficiency than DPVBi's with blue CIE value of (0.165, 0.195).

On the other hand, DPVBi has a disadvantage of low glass transition temperature(T_g) of 64°C. [11] We believe crystallization or melting of amorphous organic materials caused by Joule heating or short-circuit current accelerates device degradation. [12] To increase life time of OLED device, organic emitting materials should have high T_g as much as it can. EML 4 exhibited high T_g of 155°C and melting temperature(T_m) of 374°C.

	EML 2	EML 3	EML 4	EML 5	DPVBi
EL _{max} (nm)	492	478	475	463	458
Voltage (V)	8.9	9.0	8.1	9.5	8.6
L.E. (cd/A)	5.02	2.31	10.33	5.03	3.24
P.E. (lm/W)	1.78	0.81	4.00	1.67	1.19
C.I.E (x, y)	0.236, 0.412	0.218, 0.335	0.195, 0.303	0.165, 0.195	0.152, 0.142

Table 2. Performance characteristics of multi layer device ITO/ 2-TNATA(60nm)/ NPB(15nm) / EML 2 ~ 5 or DPVBi(30nm)/ Alq₃(30nm)/ LiF(1nm)/ Al (200nm) at 10mA/cm². L.E. =Luminance efficiency, P.E. =Power efficiency

Further studies of modified tetra-substituted ethylene synthesis and the related EL device including life time are underway.

4. Conclusion

We demonstrated the new blue emitting materials with high EL efficiency by using fully substituted ethylene moiety.

BPBAPE[EML 4] having high T_g of 155°C showed luminance and power efficiency of 10.33cd/A and 4.0 lm/W without doping agent. BTBPPA[EML 5] exhibited 5cd/A and 1.67lm/W efficiency with blue CIE value of (0.165, 0.195).

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