

# Fully Substituted Ethylene as a New Class of Efficient Sky-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. TBBPE[EML 2] device showed bluish-green CIE value of (0.236, 0.412) and 5.02cd/A at 10mA/cm<sup>2</sup>. BPBBPE[EML 3] device also showed sky-blue CIE value of (0.218, 0.355) and 2.31cd/A at 10mA/cm<sup>2</sup>.

**Keywords** : OLED, fully substituted ethylene, electroluminescence, McMurry reaction, blue emitting materials

## 1. Introduction

Organic light-emitting diodes (OLEDs) based on organic molecules are currently the subject of extensive research efforts due to their promising characteristics as devices for full-color large display applications [1-3]. To date, numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence (EL) ranging from red to green and blue [4-10]. For example, blue emitting materials have been used to commercial products such as color mobile phone and MP3 display. Even though it is, display module manufacturer still asks to develop the high EL performance of blue emitting materials. Moreover it is not easy to achieve highly efficient blue materials with a new chemical structure.

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

<sup>1</sup>H 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 with a scanning rate of 100mV/s. The compound was dissolved in DMF with 0.1M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated Ag/AgNO<sub>3</sub> reference electrode. Ferrocene was used for potential calibration.

For EL device, EML1~EML3 were vacuum-deposited on top of NPB(15 Å)/2-TNATA (600 Å)/ITO(1200 Å/30 ohm) under 10<sup>-6</sup> torr with the deposition rate of 1 Å/sec to give an emitting area of 4mm<sup>2</sup> 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.

Manuscript received October 10, 2006; accepted for publication March 15, 2007.

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-041-D00378).

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## 2.2 Synthesis

### 2.2.1 1,1,2,2-tetrakis(4'-tert-butyl-phenyl)ethene [TBPE, EML 1]

Bis(4-tert-butylphenyl) methanone(2g, 6.8mmol) and Zn powder (1.06g, 17mmol) were added to dried THF solvent(150mL), then TiCl<sub>4</sub> (1.5mL,13.6mmol) was added into the reaction mixture. The mixture was heated to 60°C for 1h under nitrogen. After the reactant mixture had cooled, it was extracted with diethyl-ether. The organic material was dried with anhydrous MgSO<sub>4</sub> and filtered, and the solution was evaporated. The residue was dissolved in CHCl<sub>3</sub> and added to methanol. The precipitate was filtered and washed with methanol.

The yellowish powder was purified by using column chromatography with CHCl<sub>3</sub> : n-hexane (1:1) eluent to afford a white solid(TBPE) (1.5g, 79%)

<sup>1</sup>H NMR : δ: 6.93(d, 8H), 7.06(d, 8H), 1.25 (s, 36H)

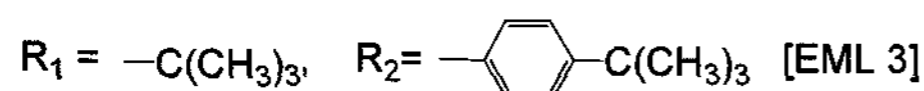
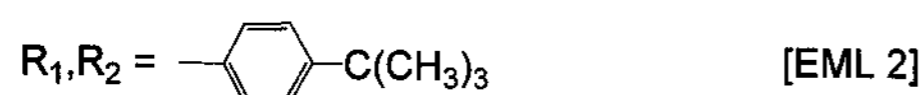
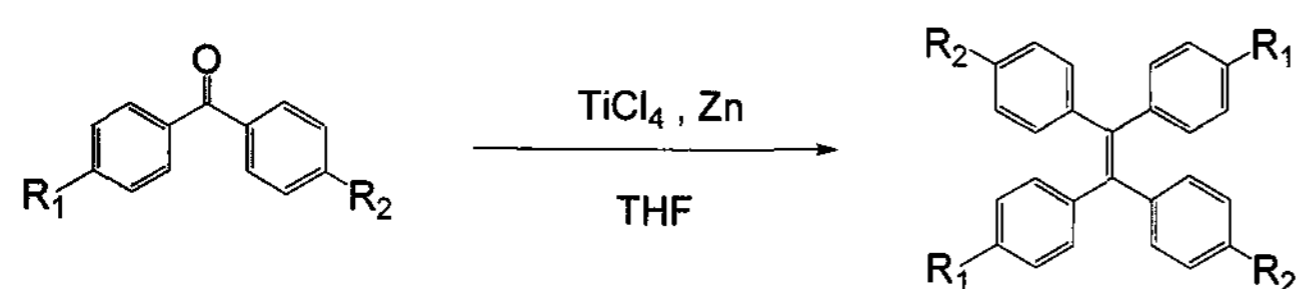
### 2.2.2. 1,1,2,2-tetrakis(4'-tert-butyl-biphenyl) ethene [TBBPE, EML 2] and 1,2-di(4'-tert-butyl-phenyl)-1,2-bis(4'-tert-butyl-biphenyl)ethane [BPBBPE, EML 3]

EML 2 was obtained by using Bis(4'-tert-butyl-biphenyl)methanone(2g, 4.5mmol) for the McMurry reaction. (1.2g, 63%)

<sup>1</sup>H 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%)

<sup>1</sup>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)



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

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 in Scheme 1, carbonyl peak at around 1645cm<sup>-1</sup> in IR completely disappeared in compounds.

## 3. Result and Discussion

Fig.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 π→π\* transition of conjugated double bond. 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 understood by the longer conjugation length of the material.

PL maximum value of EML 3 was 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.

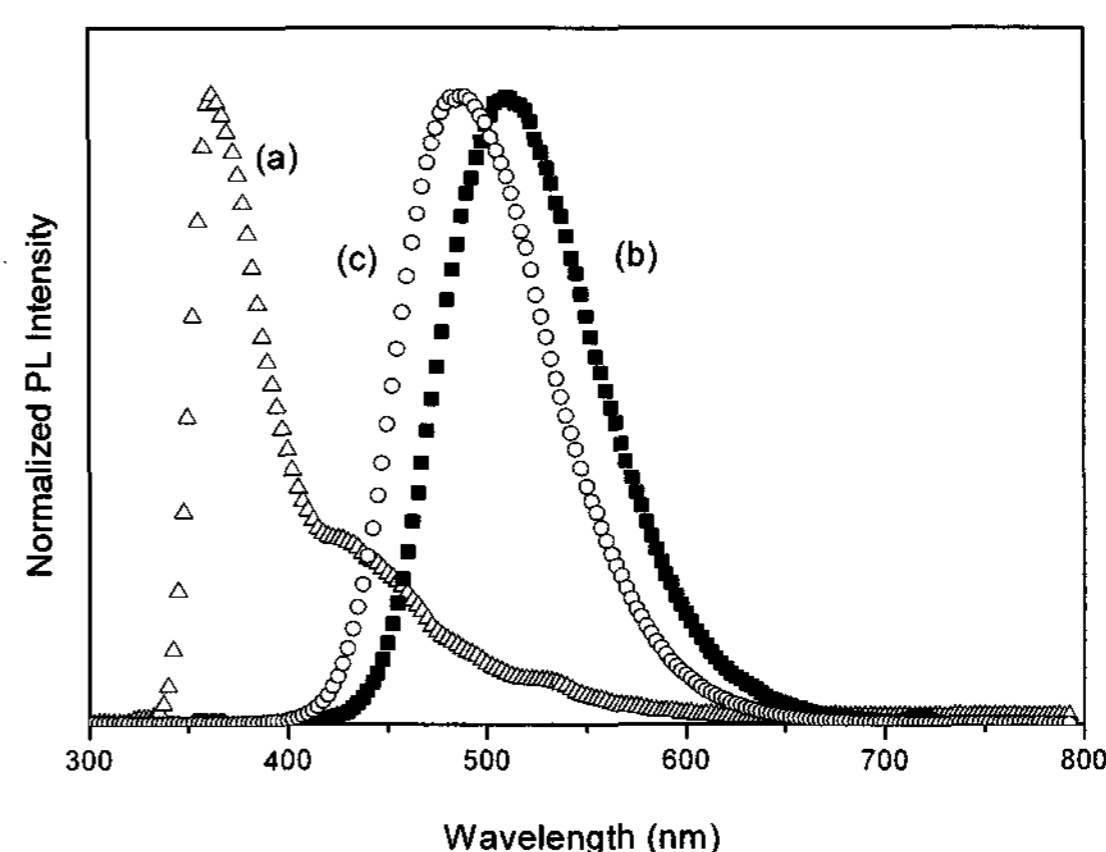


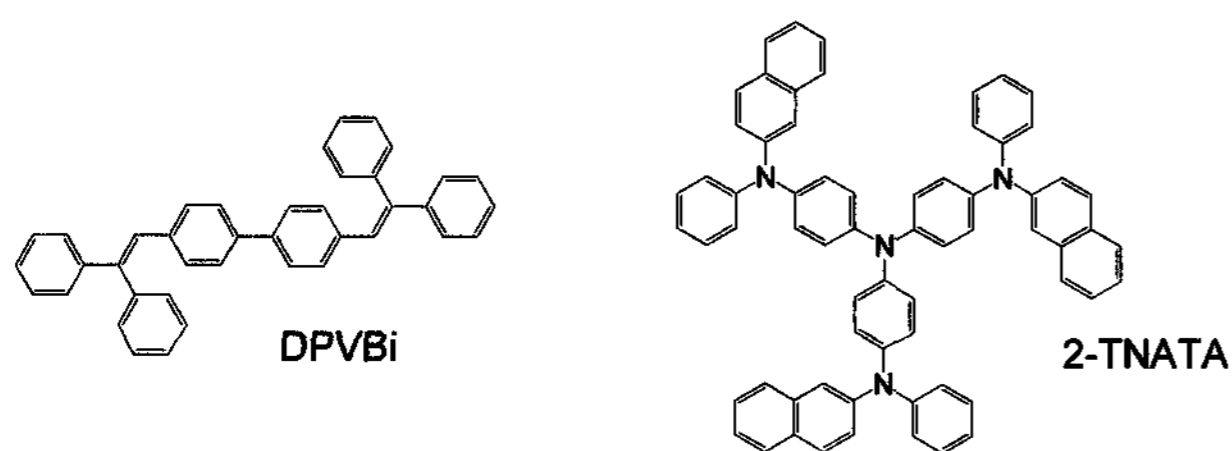
Fig. 1. PL spectra of EML 1 (△, a), EML 2 (■, b) and EML 3 (○, c)

Table 1. Absorption, emission spectra maxima and energy values of EML 1 ~ 3

	UV (nm)	PL (nm)	HOMO (eV)	LUMO (eV)	E <sub>g</sub> (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

The energy band gaps and HOMO, LUMO levels of EML 1~3 were estimated by cyclic voltammograms(CV) and the analysis of absorption edge with a plot of  $(hv)$  vs.  $(\alpha hv)^2$ , where  $\alpha$ ,  $h$ , and  $\nu$  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 are summarized in Table 1.

EL devices were fabricated in the form of ITO/ 2-TNATA(60nm)/ NPB(15nm)/ EML 1 ~ 3(30nm)/ Alq<sub>3</sub> (30nm)/ LiF(1nm)/ Al(200nm). 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

Fig. 2 shows the I-V characteristics of these devices. EML 1 showed no EL light in the device. It might be

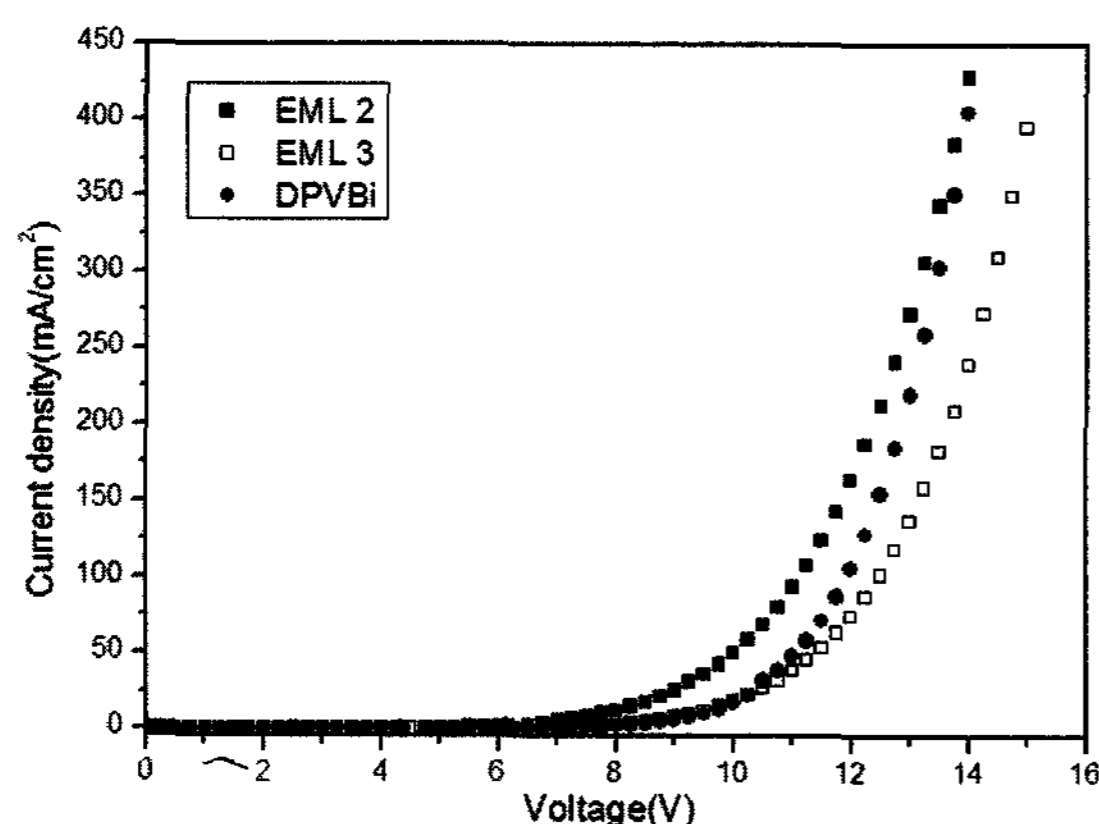


Fig. 2. I-V characteristics for ITO/ 2-TNATA (60nm)/ NPB(15nm)/ EML 2 (■) or EML 3(□) or DPVBi(○) (30nm)/ Alq<sub>3</sub> (30nm)/ LiF(1nm)/ Al(200nm) device.

due to the large energy barrier between high LUMO level (1.84eV) of EML 1 and Alq<sub>3</sub>(3.1eV) and low quantum efficiency of EML 1. It corresponds with that PL intensity of EML 1 is also about 20 times weaker than EML 2 and 3s. EML 2 device showed lower turn on voltage than EML 3, because there is relatively lower energy barrier, 0.86eV not 1.1eV between Alq<sub>3</sub> LUMO level(3.1eV) and EML 2's LUMO level(2.24eV) compared to EML 3's LUMO level(2.0eV).

Fig. 3 shows EL maximum value at 492nm or 478nm in ITO / 2-TNATA(60nm) / NPB(15nm) / EML 2 or EML 3(30nm) / Alq<sub>3</sub>(30nm)/ LiF(1nm) / Al(200nm) device. The shifted EL maximum value of 10 to 20nm from PL was observed in the devices, but the explanation of shifted EL maximum value is not clear.

EL maximum value of EML 3 was blue-shifted about 14nm from EML 2's, because of shorter conjugation length.

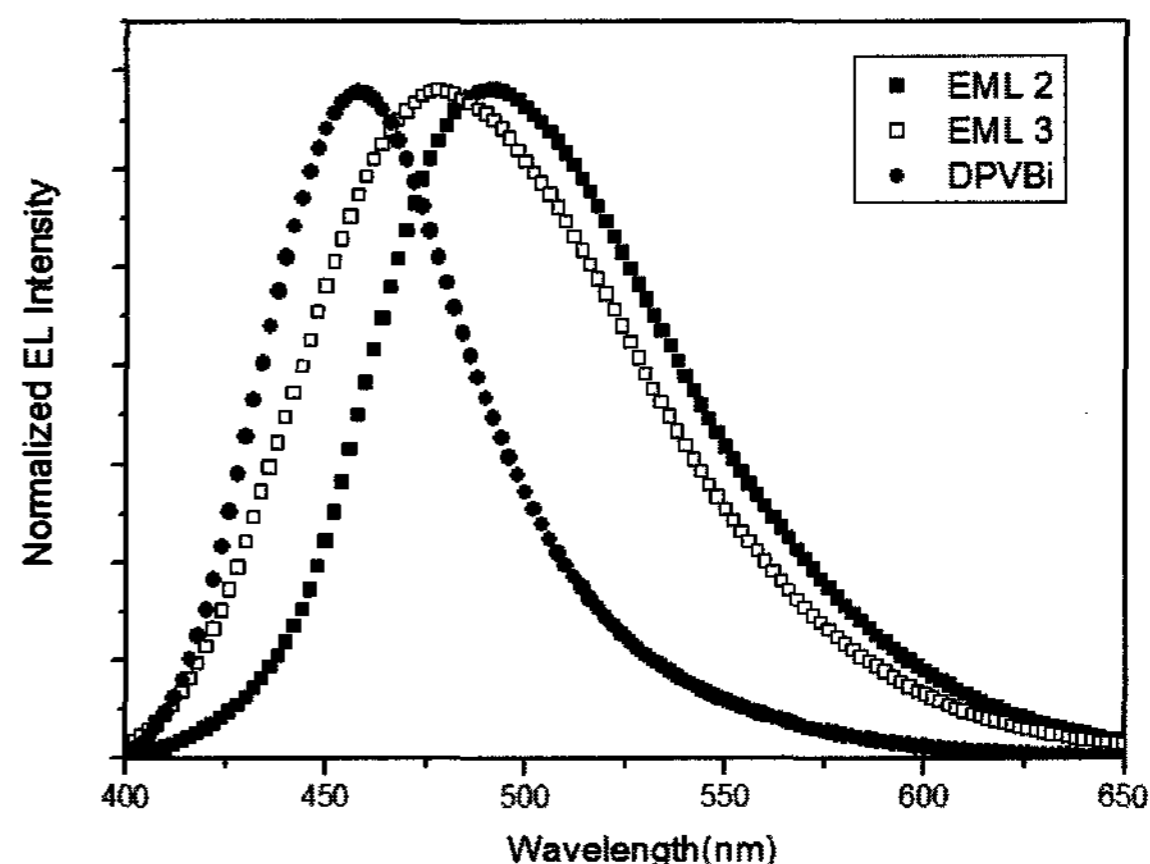


Fig. 3. EL spectra of ITO/ 2-TNATA (60nm)/ NPB(15nm)/ EML 2 (■) or EML 3(□) or DPVBi(○) (30nm)/ Alq<sub>3</sub> (30nm)/ LiF(1nm)/ Al (200nm) device.

Table 2. Performance characteristics of multi layer device ITO/ 2-TNATA(60nm)/ NPB(15nm)/ EML 2 ~ 3 or DPVBi(30nm)/ Alq<sub>3</sub>(30nm)/ LiF(1nm)/ Al(200nm) at 10mA/cm<sup>2</sup>. L.E.= Luminance efficiency, P.E. =Power efficiency

	EML 2	EML 3	DPVBi
EL <sub>max</sub> (nm)	492	478	458
Voltage(V)	8.9	9.0	8.6
L.E.(cd/A)	5.02	2.31	3.24
P.E.(lm/W)	1.78	0.81	1.19
C.I.E(x, y)	0.236, 0.412	0.218, 0.335	0.152, 0.142

**Table 3.** EL performance of multi-layered device at difference current density: ITO /2-TNATA(60nm) /NPB(15nm) /EML 2 ~ 3 or DPVBi(30nm) /Alq<sub>3</sub>(30nm) /LiF(1nm) /Al(200nm).

Current density (mA/cm <sup>2</sup> )	EML 2		EML 3		DPVBi	
	cd/A	lm/W	cd/A	lm/W	cd/A	lm/W
10	5.02	1.78	2.31	0.81	3.24	1.19
25	4.43	1.36	2.22	0.69	3.12	1.09
50	3.85	1.06	2.07	0.59	2.91	0.95
100	2.52	0.61	1.91	0.49	2.65	0.76

We summarized EL performance in Tables 2 and 3. EML 2 show bluish-green CIE value of (0.236, 0.412) and 5.02cd/A at 10mA/cm<sup>2</sup>. EML 3 also showed sky-blue CIE value of (0.218, 0.355) and 2.31cd/A at 10mA/cm<sup>2</sup>. EML 1 which connected four phenyl rings with ethylene moiety, showed no EL light and EML 3 consists of half the segments of EML 1 and EML 2. That is why EML 3 showed about half EL efficiency of EML 2 device.

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

#### 4. Conclusion

We demonstrated the new blue emitting materials with high EL efficiency by using fully substituted ethylene moiety. 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 bond. Three compounds also showed different PL maximum values as 413nm (TBPE), 511nm (TBBPE) and 489nm (BPBBPE) because of their different conjugation length.

EML 2 showed bluish-green CIE value of (0.236, 0.412) and 5.02cd/A at 10mA/cm<sup>2</sup>. EML 3 also showed sky-blue CIE value of (0.218, 0.355) and 2.31cd/A at 10mA/cm<sup>2</sup>.

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