

Synthesis and Characterization of Light-Emitting Oligo(*p*-phenylene-vinylene)s and Polymeric Derivatives Containing Three- and Five-Conjugated Phenylene Rings.

II. Electro-Optical Properties and Optimization of PLED Performance

HONG-CHEU LIN,^{1*} CHIEN-MIN TSAI,¹ YU-TAI TAO²

¹Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan, Republic of China

²Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

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ABSTRACT: A series of multilayer polymeric light-emitting diodes (PLEDs) containing an electron-transporting layer (ETL), that is tris(8-quinolinolato)-aluminum(III) (Alq) and 2,2',2''-(1,3,5-phenylene)-tris[1-phenyl-1H-benzimidazole] (TPBI), were fabricated by doping fluorescent oligo(*p*-phenylene-vinylene)s (BIII and BV) and polymer derivatives (PBV) into poly(*N*-vinyl carbazole) (PVK). These PLEDs can be optimized by the design of multilayer device configurations (brightness increased 8–15 times by addition of ETL) and possess greenish electroluminescent (EL) spectra peaked about 500–540 nm. A remarkably high brightness of 56,935 cd/m² with a power efficiency of 3.25 lm/W was obtained in the device of PVK:BVOC₈-OC₈ (100:20)/Alq (60 nm/60 nm). It suggests that the emission mechanism (including the conjugated and excimer emissions of BVOC₈-OC₈ emitters) originates from both of BVOC₈-OC₈ and ETL (Alq and TPBI) by varying the concentration of chromophores and adjusting the thickness of ETL. The concentration effect of the emitters in PVK (i.e. PVK:BVOC₈-OC₈ = 100:5, 100:20, and 100:100 wt %) and the influence of the ETL (including its thickness) on the EL characteristics are also reported. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 2922–2936, 2006

Keywords: electron-transporting layer (ETL); oligo(*p*-phenylene-vinylene)s; poly(*N*-vinyl carbazole) (PVK)

INTRODUCTION

During the last few years, the studies of the emission properties of molecular electroluminescent diodes have gained much attention.^{1–4} Polymer light-emitting diodes (PLEDs) and organic LEDs (OLEDs) can be modified and applied to LED

technologies. In PLED^{5–7} devices, electrons and holes are injected from opposite electrodes and are combined to form either singlet or triplet excitons.⁸ Because triplet radiative decay is typically forbidden in organic materials⁹ and spin statistics implies that the ratio of triplets to singlets is 3:1, even 100% photoluminescence (PL) efficiency from the singlet excitations can result only in a maximum internal quantum efficiency of 25% for electroluminescence (EL). Transition metal complexes have attracted interest in fabrication of

Correspondence to: H.-C. Lin (E-mail: linhc@cc.nctu.edu.tw)

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OLEDs, originally from the expectation that they could overcome the maximum 25% theoretical efficiency by singlet–triplet mixing.^{10–12} As a result, EL quantum efficiencies as high as 50% have been reported.¹³

For pure polymeric LED systems, a maximum luminescence of 100,000 cd/m² was found in poly(phenylene vinylene)s.¹⁴ However, polymer blend systems are easy to adjust their EL characteristics and doped PLED devices with efficient brightness are described in the following examples. For instance, in polymer blend systems containing poly(*N*-vinyl carbazole) (PVK) ($M_w = 1000,000$) as the matrix, poly[4,4'-biphenylene- α -(9'',9''-dihexyl-3-fluorenyl)vinylene] (PBPHFV) doping device (PBPHFV:PVK = 1:5)^{15,16} can reach up to a brightness of 9342 cd/m² and poly[9,9-bisocetyl]-fluorene-2,7-diyl] (PF) doping device (PF:PVK = 1:100) can attain a brightness about 8300 cd/m².¹⁷ Besides, green light emission for electrophosphorescent OLEDs with an external quantum ($Q_{\text{ext.}}$) efficiency of 19.2% and a luminescence efficiency of 73 cd/A at a current density (j) of 0.55 mA/cm² were reported in the device containing perfluorinated phenylene as a both hole- and exciton-blocking layer, and a hole-transporting host 4,4',4''-tri(*N*-carbazolyl)triphenylamine doped with a phosphorescent dye [Ir(ppy)₃] as an emitting layer.¹⁸ Furthermore, if [Ir(ppy)₃] dyes are doped into PVK in a triple-layer device configuration, $Q_{\text{ext.}}$ efficiency = 7.5% is reported.¹⁹ Moreover, phosphorescent tris(4,7-diphenyl-1,10-phenanthroline) rhenium complexed with various doping ratios of phosphorescent [Ir(ppy)₃] in doubly doped PVK systems can modify the driving voltage.^{20–22} In addition, for green light emission, the full width at half maximum (FWHM) and lifetime of an efficient OLED device, which contains TPBI as an electron-transporting material and a fluorescent {6 *N,N*-diethylamino-1-methyl-3-phenyl-1H-pyrazolo[3,4-*b*]quinoline} as a dopant in the hole-transporting layer of NPB, are measured to be 60 nm and 10,000 h, respectively.²³ Another electrophosphorescent device with fac-tris(2-phenylpyridine)iridium as a green dopant emitter and aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BALq) as a hole-blocking material demonstrates an efficiency of 19 cd/A with a projected operational lifetime of 10,000 h, or 50,000 h normalized to 100 cd/m².²⁴ In the meanwhile, doping devices of red and white EL with high brightness were developed, for example 6800 cd/m² in Ir complexes-based OLED²⁵ and 20,000 cd/m² in (ITO/PEDOT/PF:TBH/LiF/Ca) PLED²⁶ devices.

Previously, a series of light-emitting oligo(*p*-phenylene-vinylene)s (BIII and BV) and polymer derivatives (PBV) have been reported.²⁷ Because of the poor film quality of these chromophores, OPVs and poly(*p*-phenylenevinylene)s were doped into PVK to form various blend films in a PVK matrix (chromophore/PVK = 1:100 wt %), which were applied to PLED devices. Although the blend films containing three-conjugated ring oligomers can only have the highest brightness of 120 cd/m² or so, they can be further improved to have brightness greater than 50,000 cd/m² by the optimization of electro-optical properties. Related results by introduction of hole- and electron-transporting layers in the multilayer design of PLED devices will be reported in this article, where Alq and TPBI are utilized as electron-transporting layers (ETLs) to obtain high brightness and efficiencies. The characteristics of PLED devices are explored by changing the concentration of dopants in PVK and by adjusting various thicknesses of electron-transporting layers. The PLED devices are also investigated by blending NPB hole-transporting dopants into the emitting layer or by inserting a hole-blocking layer of BCP between the emitting layer and the ETL (Alq). The result shows that mesogenic BV derivatives with proper alkoxy groups possess excellent hole-transporting property and high brightness in PLED devices, which contain an electron-transporting Alq layer (or Alq as an emitting layer simultaneously). In general, the photophysical characteristics, including brightness and efficiency, of these PLEDs can be much improved by the multilayer design of device configurations.

EXPERIMENTAL

The solutions (30 mg/mL) of light-emitting materials in 1,2-dichloroethane were spin-coated on glass slides precoated with indium tin oxide (ITO) with sheet resistances of $\sim 20 \Omega/\text{square}$ and with an effective individual device area of 3.14 mm². The ITO glasses were routinely cleaned by ultrasonic treatment in detergent solutions and diluted water, followed by through rinsing in acetone and then ethanol. After drying, the ITO glasses were kept in oxygen plasma for 3 min before being loaded into the vacuum chamber. The doping concentrations of emitters in PVK were 5:100, 20:100, and 100:100 (emitter:PVK) wt %. The spin coating rate was 3000 rpm for 40 s, and the thickness of the emitting layer was about

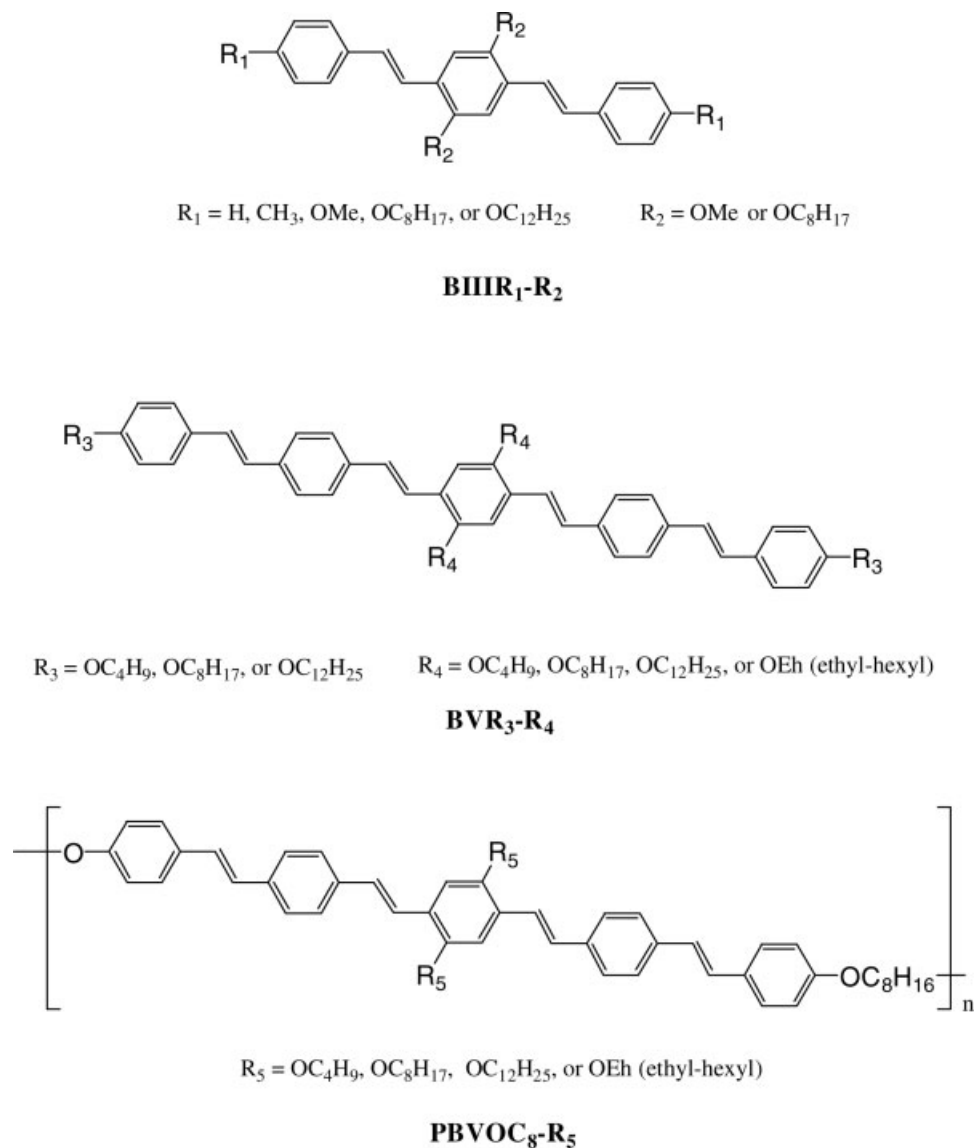


Figure 1. Molecular structures of fluorescent oligo(*p*-phenylene-vinylene)s (BIII and BV) and polymer derivatives (PBV).

60 nm (with a total thickness of 100 nm, including 40 nm of TPBI or Alq). The organic layers of small molecules were deposited thermally at a rate of 0.1–0.3 Å/s under a pressure of $\sim 2 \times 10^{-5}$ torr in an Ulvac Cryogenic deposition system. One layer of magnesium and silver alloy ($\sim 10:1$, 50 nm) was deposited as a cathode, which was capped with 100 nm of silver. The current–voltage–luminescence properties were measured in ambient conditions with a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with an 818ST silicon photodiode. The optical band gap (E_g) and highest occupied molecular orbital (HOMO) values were measured by UV–vis (solution) and AC2 (powder), respectively. Then, the

lowest unoccupied molecular orbital (LUMO) values can be calculated from the HOMO and E_g values. The synthetic procedures of TPBI and Alq were reported in the literature.²³

RESULTS AND DISCUSSION

The device configuration and molecular structures of emitters and materials used in the PLED devices are shown in Figures 1 and 2. The synthesis and physical characterization of light-emitting oligo(*p*-phenylene-vinylene)s (BIII and BV) and polymer derivatives (PBV) have been reported previously.²⁷

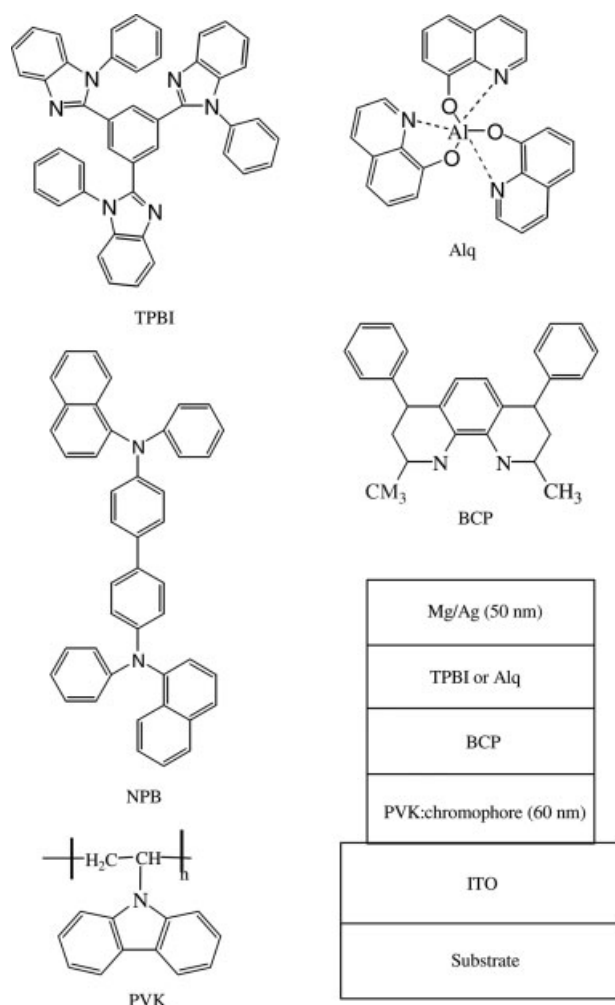


Figure 2. PLED device configuration and molecular structures of materials used in this study.

The EL characteristics of PLED devices containing BV derivatives with five-conjugated rings are shown in Table 1. Among all the fluorescent oligo(*p*-phenylene-vinylene)s (BIII and BV) and polymer derivatives (PBV), BVOC₈-OC₈ is the brightest (EL) compound in this study. With regard to the PLED device of PVK:BVOC₈-OC₈ (100:20)/Alq (60 nm), the maximum luminescence (EL) = 56,935 cd/m² and the FWHM = 92 nm, CIE (*x,y*) = (0.34,0.59), and the wavelength of maximum emission = 536 nm are obtained. As light-emitting BVOC₈-OC₈ is the brightest EL compound, related EL properties of various PLED device configurations regarding BVOC₈-OC₈ emitters are surveyed.

The concentration effects of BVOC₈-OC₈ emitters on PL spectra in solution and blend film states are demonstrated in Figures 3 and 4, respectively. In addition to pure films, the PL

Table 1. EL Characteristics of Various PLED Devices Containing BV Derivatives and ETL (40 nm) of Alq or TPBI

Chromophore (ETL)	BVOC4-OC4 ^a (Alq/TPBI)	BVOC4-OC8 ^a (Alq/TPBI)	BVOC4-OC8 ^a (Alq/TPBI)	BVOC4-OC12 ^a (Alq/TPBI)	BVOC8-OC8 ^a (Alq/TPBI)	BVOC8-OC8 ^a (Alq/TPBI)	BVOC8-OC12 ^a (Alq/TPBI)	BVOC8-OC8 ^a (Alq/TPBI)	BVOC8-OC8 ^b (Alq/TPBI)	BVOC8-OC8 ^c (Alq/TPBI)
Turn-on voltage (V)	2.4/3.5	3.1/3.8	2.3/3.0	2.2/3.3	2.9/3.0	3.1/3.1	3.1/3.2	3.0/3.0	3.5/3.2	2.2/2.9
Max. brightness, (cd/m ²)	15,935/7,362	32,592/12,306	22,495/8,096	18,551/8,790	50,144/27,328	26,855/9,494	15,569/10,679	46,633/16,710	17,334/22,578	25,280/28,868
Max. external quantum eff. (%)	1.7/2.0	1.4/0.5	1.4/1.1	1.6/1.9	2.0/1.6	1.0/1.1	0.9/1.9	0.8/0.7	0.5/1.8	3.1/2.9
Max. power eff. (lm/W)	1.2/1.4	1.6/0.4	1.5/0.7	1.8/1.4	2.9/2.5	0.9/1.1	1.0/1.1	0.9/0.7	1.0/1.4	4.0/3.7
λ _{em} (FWHM) (nm) (EL)	524 (86)/504 (78)	528 (80)/512 (84)	520 (86)/512 (76)	516 (86)/500 (76)	534 (84)/534 (66)	512 (80)/506 (68)	512 (88)/494 (94)	538 (72)/538 (70)	518 (88)/504 (70)	538 (68)/538 (68)
CIE, (<i>x,y</i>)	0.29, 0.55/0.21, 0.44	0.30, 0.61/0.31, 0.60	0.29, 0.59/0.26, 0.61	0.27, 0.57/0.21, 0.47	0.33, 0.61/0.30, 0.62	0.28, 0.58/0.24, 0.55	0.26, 0.54/0.18, 0.33	0.35, 0.60/0.36, 0.60	0.28, 0.56/0.23, 0.54	0.36, 0.62/0.36, 0.60
Voltage at 100 mA/cm ² (V)	12.4/14.1	13.9/18.3	14.2/22.0	12.7/16.0	11.6/9.6	12.2/13.4	11.7/14.2	13.6/13.2	12.4/12.5	14.1/12.8
Brightness at 100 mA/cm ² (cd/m ²)	4,710/2,721	5,059/1,573	4,656/2,618	5,045/2,602	6,867/5,619	3,475/2,466	2,908/2,615	2,695/2,776	3,097/5,340	11,545/10,937
External quantum eff. at 100 mA/cm ² (%)	1.7/1.2	1.4/0.4	1.3/0.7	1.5/1.0	1.8/1.6	1.0/0.8	0.9/1.3	0.7/0.7	0.5/1.8	2.7/2.8
Power eff. At 100 mA/cm ² (lm/W)	1.2/0.6	1.1/0.3	1.0/0.4	1.3/0.5	1.9/1.9	0.9/0.6	0.8/0.6	0.6/0.7	0.8/1.4	2.6/2.7

^a The thickness of Alq or TPBI is 40 nm and PVK:chromophore = 100:20.

^b The thickness of Alq or TPBI is 40 nm and PVK:chromophore = 100:5.

^c The thickness of Alq or TPBI is 40 nm and PVK:chromophore = 100:100.

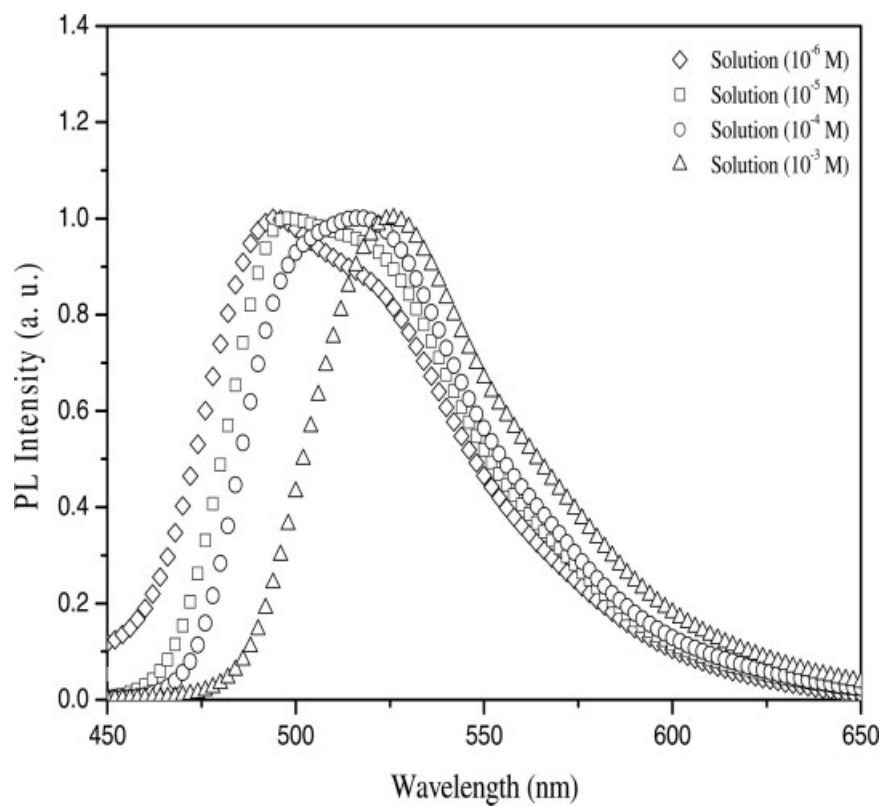


Figure 3. PL spectra of BVOC₈-OC₈ in solutions (dichloroethane as solvent) with various concentrations.

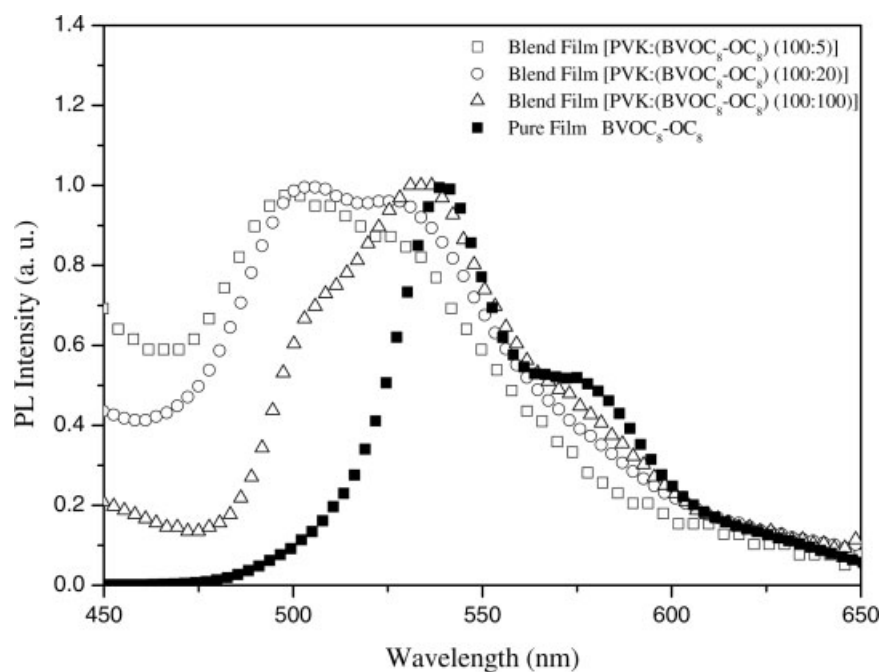


Figure 4. PL spectra of BVOC₈-OC₈ in pure and blend films.

spectra of BVOC₈-OC₈ blended in PVK with various concentrations, that is PVK:BVOC₈-OC₈ = 100:5, 100:20, and 100:100 wt %, are measured in the film states (see Fig. 4). Owing to the aggregation of chromophores, the λ_{max} values of PL emission peaks are all red-shifted at higher concentrations in solution and film states, which are also observed in the EL spectra of Figure 5. Nonetheless, the PL emission of PVK (~ 400 nm) in Figure 4 is more obvious (i.e. the lower the concentration of the chromophore, the higher is the PL emission peak of PVK relative to the maximum PL emission peak of BVOC₈-OC₈) than the EL emission of PVK in Figure 5. As described in the literature, Ir(DPPF)₃ emitters doped in PVK matrix,²⁸ the absence of PVK EL emission from devices of BVOC₈-OC₈ (doped in PVK matrix with various concentrations) may be due to the charge trapping of BVOC₈-OC₈ emitters, rather than Förster transfer, as the dominant mechanism in these PLED Devices. If energy transfer was the dominant EL mechanism, the EL emission of PVK would be expected to appear when BVOC₈-OC₈ emitters become saturated. As revealed by Figure 3, the red-shifted PL emissions originated from the aggregation of chromophores at higher concentrations are verified by the PL emission of BVOC₈-OC₈ solution with various concentrations in dichloroethane. Hence, the excimers are formed

as the concentration of light-emitting materials (i.e. BVOC₈-OC₈) increases, and additional red shifts of λ_{max} values in BVOC₈-OC₈ PL emissions are further confirmed by increasing the concentration of BVOC₈-OC₈ in PVK (see Fig. 4). The PL spectrum of the pure film has the longest λ_{max} value (along with an obvious shoulder about 570 nm) because of the largest aggregation of emitters in the film state, and the PL spectrum (excluding the PVK emission) in the blend film of PVK:BVOC₈-OC₈ = 100:5 wt % is similar to those of dilute solutions at 10^{-5} – 10^{-6} M. Therefore, most BVOC₈-OC₈ molecules in PVK matrix could be dispersed well in the blend film of PVK:BVOC₈-OC₈ = 100:5 wt %, and so the charge hopping would occur mainly between the molecules. However, in PLED devices of PVK:BVOC₈-OC₈ = 100:20 and 100:100 wt %, higher concentrations would cause larger electronic interaction²⁹ among most BVOC₈-OC₈ molecules because of the decreased separation between them. As a result, the charges injected from two opposite electrodes would transport and recombine mainly on these sites.

Since PVK is used as matrices in this study, the EL emission PVK is not observed in the EL spectra of blend film devices, and the PVK PL emission is not overlapped with the major emission peaks in the PL spectra of blend films (see Fig. 4). Thus, it is adequate to judge the emission

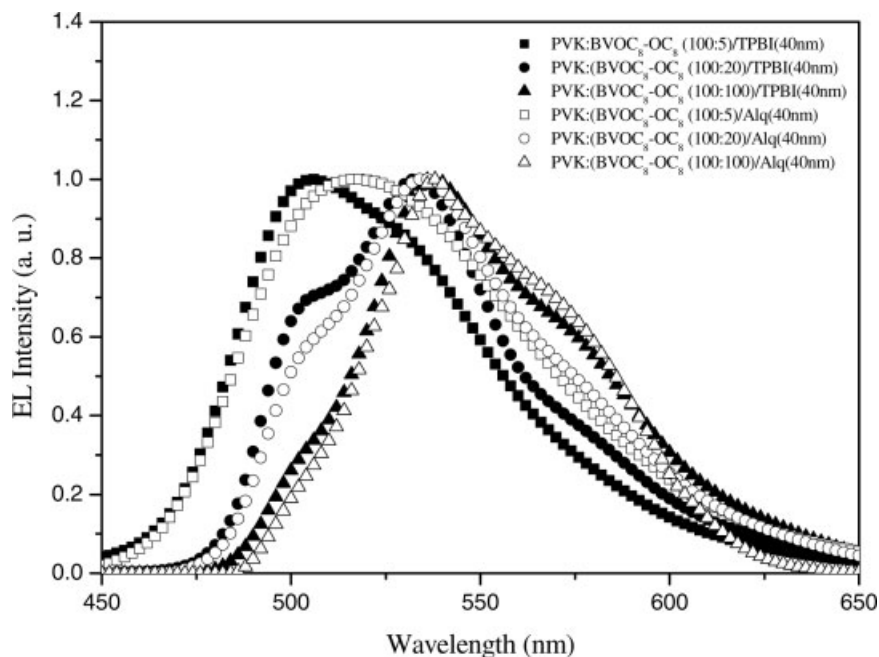


Figure 5. EL spectra of PLED devices containing Alq or TPBI (with a thickness of 40 nm) as the ETL and various concentrations of BVOC₈-OC₈ blended in PVK (with a thickness of 60 nm) as the light-emitting layer.

phenomena of these blend films and PLED devices. To improve the PLED performance, all polymer blend (with different weight concentrations of emitters in PVK matrix) devices incorporate a layer of Alq or TPBI as the electron transporter. The EL spectra of PLED devices containing Alq or TPBI (with a thickness of 40 nm) as the ETL and various concentrations of light-emitting BVOC₈-OC₈ blended in PVK (with a thickness of 60 nm) as the light-emitting layers are depicted in Figure 5. In devices with TPBI as ETL, at lower concentrations of BVOC₈-OC₈, that is PVK:BVOC₈-OC₈ = 100:5 wt %, the λ_{max} values of EL emission peaks about 500 nm and weaker shoulders (\sim 540 nm) originated from the excimers of molecular aggregation are observed. For PLED devices with higher concentrations of BVOC₈-OC₈, that is PVK:BVOC₈-OC₈ = 100:20 and 100:100 wt %, the λ_{max} values of EL emission peaks have shifted to about 540 nm because of the aggregation of chromophores at higher concentrations. The original EL emission peaks (\sim 500 nm) in the lowest concentration (i.e. PVK:BVOC₈-OC₈ = 100:5 wt %) devices becomes weak shoulders in the medium concentration (i.e. PVK:BVOC₈-OC₈ = 100:20 wt %) devices, which even diminish at the highest concentration (i.e. PVK:BVOC₈-OC₈ = 100:100 wt %) devices. Similar trend of EL spectra is observed in devices using either Alq or TPBI as the ETL (see Fig. 5). In addition, shoulders about 570 nm originated from different degrees of aggregation become more detectable in the EL spectra of higher concentrations of BVOC₈-OC₈ blended devices, which are also observable in the PL spectra of BVOC₈-OC₈ blend films in Figure 4 (especially an obvious shoulder at 567 nm observed in the pure film of BVOC₈-OC₈ because of the aggregation of the pure film state). To test the possible origin of electroplex formation in the shoulder of EL spectra in Figure 5, voltage-dependent EL spectra were measured. As the relative intensity of the main peak and the shoulder of EL spectra do not change with voltages, one can exclude the possibility of electroplex formation in these devices.

Because the blend films are solid solutions having various doping ratios of emitters in PVK, they have similar results as normal solutions. The π - π stacking effect appears in solid films to form excimers, and so when compared with solution forms, red shifts of λ_{max} values were observed. To realize the difference among the devices of BVOC₈-OC₈, PL spectra of solutions, thin films, and blend

films (emitters doped in PVK) are analyzed to confirm this assumption. The maximum emission peaks of PL spectra in pure films are seriously red-shifted because of the aggregation of π - π stacking among these three conditions (i.e. solutions, pure films, and blend films), and so it shows the largest red shift in pure films (see Fig. 4). Interestingly, as shown in Figures 3–5, the λ_{max} values of PL spectra in blend films (PVK:BVOC₈-OC₈ = 100:5 wt %) and solution (10^{-5} – 10^{-6} M) are similar to that of EL spectra (TPBI as an ETL) with the same doping concentration of BVOC₈-OC₈ (PVK:BVOC₈-OC₈ = 100:5 wt %), although the concentration of BVOC₈-OC₈ in PVK (PVK:BVOC₈-OC₈ = 100:5 wt %) is much larger than that of the solution (10^{-5} – 10^{-6} M). In general, the concentration effects of emitters on the λ_{max} values of EL devices are similar to those of PL spectra with various concentrations.

The electroluminescent properties of various PLED devices containing BV derivatives and ETL (40 nm) of Alq or TPBI are shown in Table 1. Among these PLED (PVK:BV derivatives = 100:20) devices, the device containing BVOC₈-OC₈ emitters blended in PVK has the highest brightness. By adding an ETL (with a thickness of 40 nm) of Alq or TPBI, the EL properties of PVK:BVOC₈-OC₈ = 100:20 device are much enhanced and the maximum brightness has increased 8–15 times (from 3319 without an ETL to 50,144 cd/m² by adding Alq and to 27,328 cd/m² by adding TPBI) because of the improved device configuration with an ETL. To evaluate the concentration effect of the emitters, the EL properties of PLED devices containing BVOC₈-OC₈ emitters blended in PVK with various concentrations, that is PVK:BVOC₈-OC₈ = 100:5, 100:20, and 100:100 wt %, are also compared in Table 1. Their properties of the maximum luminescence, along with the turn-on voltage and Q_{ext} efficiency, while using TPBI as an ETL (shown in Table 1) are listed according to the luminescence order: (28,868 cd/m², 2.9 V, and 2.9%) for (PVK:BVOC₈-OC₈ = 100:100 wt %), (27,328 cd/m², 3.0 V, and 1.6%) for (PVK:BVOC₈-OC₈ = 100:20 wt %), and (22,578 cd/m², 3.2 V, and 1.8%) for (PVK:BVOC₈-OC₈ = 100:5 wt %), respectively. Similar to the luminescence result, it shows the best value of Q_{ext} efficiency (2.9%) in the PLED device of (PVK:BVOC₈-OC₈ = 100:100 wt %) where TPBI may supply a proper electron transporting speed to match the hole transporting speed. However, replacing TPBI with Alq as an ETL, the concentration effect of BVOC₈-OC₈ on

Table 2. EL Characteristics of PLED Devices Containing NPB and ETL (40 nm) of Alq

	NPB/Alq (60 nm/40 nm)	PVK:NPB/Alq (100:5) (60 nm/40 nm)	PVK:NPB: BVOC ₈ -OC ₈ / Alq (100:5:20) (60 nm/40 nm)
Turn-on voltage (V)	3.2	5.3	4.2
Max. brightness (cd/m ²)	41,378	24,012	9,877
Max. external quantum eff. (%)	2.56	1.71	2.3
Max. power eff. (lm/W)	2.67	1.32	1.66
λ_{max} (FWHM) (nm) (EL)	525 (66)	526 (66)	528 (68)

EL peaks of Alq devices are similar to that of TPBI devices. Nevertheless, comparing the efficiency and brightness of PLED systems using either Alq or TPBI as an ETL, Alq is better than TPBI as Alq seems to provide multiple properties (including both roles of ETL and luminescent layer) in PVK:BVOC₈-OC₈/Alq devices. The multiple properties in luminescence will be discussed later.

As shown in Tables 2–5, to evaluate the hole-transporting capability and the emitting mechanism of the multilayer PLED devices, the EL characteristics of the doped PLED devices containing BVOC₈-OC₈ emitters are affected by adding hole-transporting NPB dopants in PVK and by the thickness of ETL (TPBI or Alq) and BCP (hole-blocking layer). The device characteristics (the maximum EL, turn-on voltage, and Q_{ext} efficiency) of PLEDs doped with hole-transporting NPB are as follows (see Table 2): (24,012 cd/m², 5.3 V, and 1.71%) for device PVK:NPB (100:5)/Alq (60 nm/40 nm); and (9877 cd/m², 4.2 V, and 2.3%) for device PVK:NPB:BVOC₈-OC₈ (100:5:20)/Alq (60 nm/40 nm). It is not clear why the complexity of the components in NPB-doped (PVK:NPB:BVOC₈-OC₈ = 100:5:20) devices may cause the

falling off in aforementioned EL properties, which may be due to the mismatch of the LUMO and HOMO energy levels in NPB and BVOC₈-OC₈. However, although the maximum EL of device PVK:NPB:BVOC₈-OC₈ (100:5:20)/Alq (60 nm/40 nm) is not as good as that of a standard device NPB/Alq (60 nm/40 nm) (41,378 cd/m², 3.2 V, 2.56%), BVOC₈-OC₈ (without NPB) can improve the luminescent properties in PLED devices. Despite the fact that PVK is a hole-transporting material, the maximum EL and Q_{ext} efficiency of PVK/Alq (60 nm/40 nm) are 10,033 cd/m² and 0.72% shown in Table 4, which are not as good as NPB/Alq (60 nm/40 nm). Furthermore, the turn-on voltage and luminescence (at 20 V) of the device without NPB, that is PVK:BVOC₈-OC₈ (100:20)/Alq (60 nm/40 nm) with (50,144 cd/m², 2.9 V, and 2.02%) revealed in Table 3, are better than those of NPB doped devices. Therefore, it is verified that BVOC₈-OC₈ is a good hole-transporting material in the previous comparison.

To evaluate the electron-transporting behavior of TPBI and Alq, the EL characteristics of PVK:BVOC₈-OC₈ (100:20)/TPBI (X nm) and PVK:BVOC₈-OC₈ (100:20)/Alq (X nm) devices with different thicknesses of ETL (TPBI or Alq),

Table 3. EL Characteristics of PVK:BVOC₈-OC₈ (100:20)/TPBI (X nm) Devices^a with Different Thicknesses of ETL (TPBI)

	PVK:BVOC ₈ -OC ₈ / TPBI (20 nm)	PVK:BVOC ₈ -OC ₈ / TPBI (40 nm)	PVK:BVOC ₈ -OC ₈ / TPBI (60 nm)
Turn-on voltage (V)	3.5	2.7	2.4
Max. brightness (cd/m ²)	18,034	26,199	27,437
Max. external quantum eff. (%)	1.13	1.55	1.71
Max. power eff. (lm/W)	1.83	2.41	2.49
λ_{max} (FWHM) (nm) (EL)	538 (60)	534 (66)	504 (80)

^a The thickness of the emitting layer is 60 nm and PVK:chromophore =100:20.

Table 4. EL Characteristics of PVK:BVOC₈-OC₈ (100:20)/Alq (X nm) Devices^a with Different Thicknesses of ETL (Alq)

	PVK:BVOC ₈ -OC ₈ /Alq (20 nm)	PVK:BVOC ₈ -OC ₈ /Alq (40 nm)	PVK:BVOC ₈ -OC ₈ /Alq (60 nm)	PVK/Alq (60 nm/20 nm)	PVK/Alq (60 nm/40 nm)	PVK/Alq (60 nm/60 nm)
Turn-on voltage (V)	2.8	2.9	3.1	4.1	3.9	3.6
Max. brightness (cd/m ²)	39,584	50,144	56,935	10,067	10,033	9,605
Max. external quantum effc. (%)	0.91	2.02	2.44	0.20	0.72	1.14
Max. power effc., (m/W)	1.02	2.93	3.25	0.43	1.51	2.43
λ_{max} (FWHM), nm (EL)	506 (78)	534 (84)	536 (92)	518 (90)	521 (90)	526 (90)

^aThe thickness of the emitting layer is 60 nm and PVK:chromophore =100:20.**Table 5.** EL Characteristics of PVK:BVOC₈-OC₈ (100:20)/BCP (X nm)/Alq(Y nm) Devices^a with Different Thicknesses of Hole-Blocking BCP Layer and ETL (Alq)

	PVK:BVOC ₈ -OC ₈ /BCP/Alq (5 nm/20 nm)	PVK:BVOC ₈ -OC ₈ /BCP/Alq (5 nm/40 nm)	PVK:BVOC ₈ -OC ₈ /BCP/Alq (5 nm/60 nm)	PVK:BVOC ₈ -OC ₈ /BCP/Alq (10 nm/20 nm)	PVK:BVOC ₈ -OC ₈ /BCP/Alq (10 nm/40 nm)	PVK:BVOC ₈ -OC ₈ /BCP/Alq (10 nm/60 nm)
Turn-on voltage (V)	3.5	3.2	3.2	4.3	3.5	3.5
Max. brightness (cd/m ²)	9,304	9,978	9,932	4,978	6,943	7,653
Max. external quantum effc. (%)	0.32	0.34	0.48	0.29	0.35	0.48
Max. power effc. (lm/W)	0.44	0.53	0.61	0.49	0.55	0.64
λ_{max} (FWHM), nm (EL)	506 (76)	506 (86)	534 (92)	504 (78)	508 (84)	530 (86)

^aThe thickness of the emitting layer is 60 nm and PVK:BVOC₈-OC₈ =100:20.

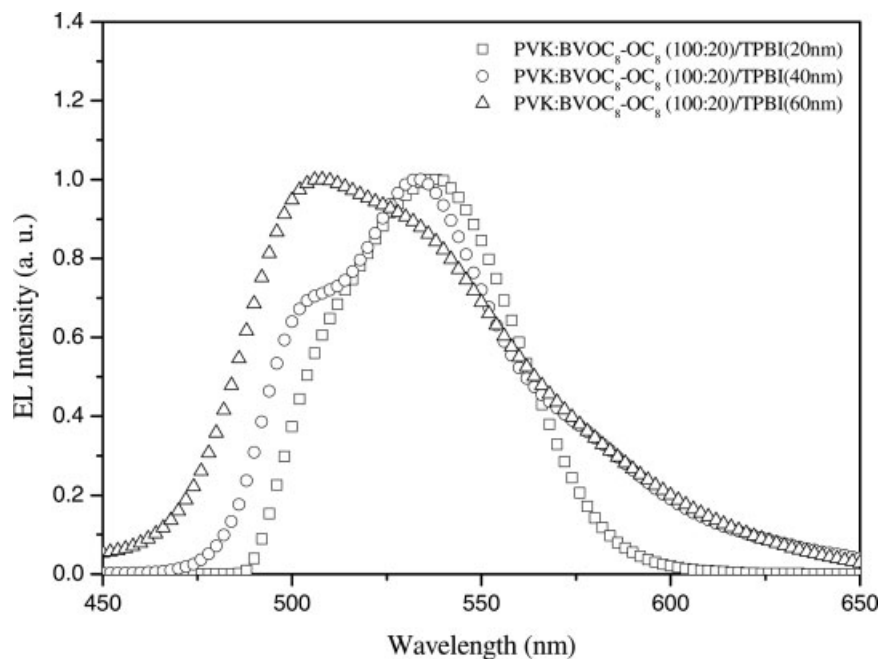


Figure 6. The EL characteristics of PVK:BVOC₈-OC₈ (100:20)/TPBI (*X* nm) devices with different thicknesses of ETL (TPBI), that is *X* = 20, 40, and 60 nm.

that is *X* = 20, 40, and 60 nm, are shown in Figures 6 and 7 and Tables 3 and 4. By decreasing the thickness of TPBI (ETL), the emission λ_{max}

values in EL spectra are red-shifted from 504 nm (as TPBI = 60 nm) to 538–534 nm (as TPBI = 20 and 40 nm), and stronger excimer emissions occur

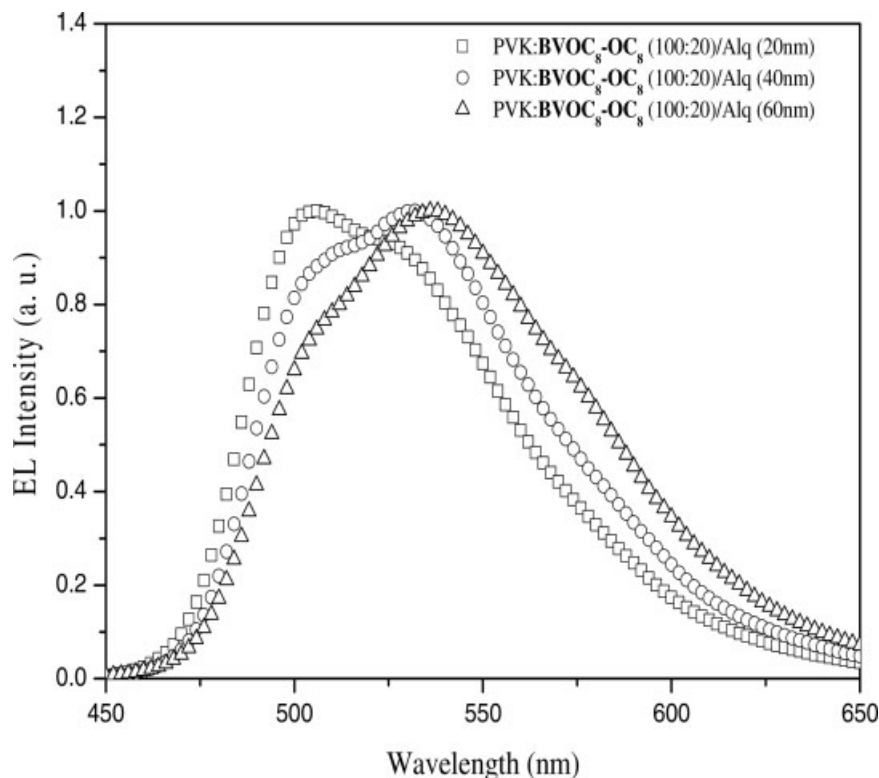


Figure 7. The EL characteristics of PVK:BVOC₈-OC₈ (100:20)/Alq (*X* nm) devices with different thicknesses of ETL (Alq), that is *X* = 20, 40, and 60 nm.

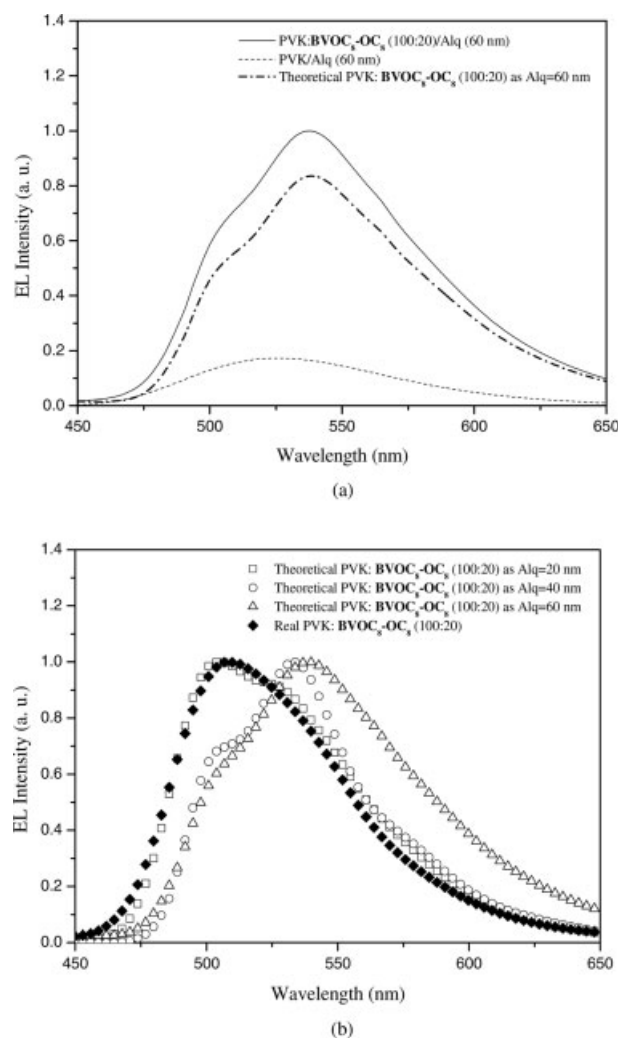


Figure 8. (a) The theoretical EL spectrum of PVK:BVOc₈-OC₈ (100:20) is obtained from the EL spectra of PVK:BVOc₈-OC₈ (100:20)/Alq (60 nm) minus that of PVK/Alq (60 nm). (b) The theoretical EL spectra of PVK:BVOc₈-OC₈ (100:20) obtained from devices of PVK:BVOc₈-OC₈ (100:20)/Alq (*X* nm), where the thicknesses of Alq (*X* nm) is 20, 40, and 60 nm, respectively, and the real EL spectrum of PVK:BVOc₈-OC₈ (100:20) are compared.

as TPBI = 20 and 40 nm. As the EL emission peaks of PVK and TPBI are about 400 nm, the EL spectra and characteristics of PVK:BVOc₈-OC₈ (100:20)/TPBI (*X* nm) illustrated in Figure 6 and Table 3 are mainly from BVOc₈-OC₈ emitters. The excimer emission has more contribution by the device configuration of thinner ETL of TPBI (as TPBI = 20 and 40 nm); however, the major EL emission peak ($\lambda_{\text{max}} = 504$ nm) in the device with thicker ETL of TPBI (as TPBI = 60 nm) is similar to that without TPBI [$\lambda_{\text{max}} = 508$ nm shown in Ta-

ble 1 and Fig. 8(b)], where the excimer emission is suppressed. On the other hand, by increasing the thickness of Alq (ETL), the EL emission λ_{max} values are red-shifted from 506 nm (Alq = 20 nm) to 534–536 nm (Alq = 40 and 60 nm) shown in Figure 7 and Table 4. Since the EL emission peak of Alq is about 518–526 nm (see the device of PVK/Alq in Table 4), the red shift of EL emission peak (from 506 nm to 534–536 nm) in the device of PVK:BVOc₈-OC₈ (100:20)/Alq (*X* nm) may be enhanced by increasing the thickness of Alq, which may be due to stronger EL emissions of thicker Alq or excimer emissions of BVOc₈-OC₈ emitters. Besides, higher maximum brightnesses and Q_{ext} efficiencies of PLEDs are obtained by increasing the thickness (i.e. from 20 nm to 40 and 60 nm) of ETL (either Alq or TPBI) (Tables 3 and 4).

Since Alq provides multiple properties (including both roles of ETL and luminescent layer) in PVK:BVOc₈-OC₈/Alq devices, the emission ratios between BVOc₈-OC₈ and Alq are analyzed. The theoretical EL spectrum of PVK:BVOc₈-OC₈ (100:20) device is shown in Figure 8(a) by the subtraction of the EL spectrum of PVK/Alq (60 nm) from that of PVK:BVOc₈-OC₈ (100:20)/Alq (60 nm). The ratio of emission by BVOc₈-OC₈ *versus* Alq can be obtained from the integration areas of EL spectra, and so the EL emission ratio of BVOc₈-OC₈ and Alq is 5:1 for theoretical EL emission of PVK:BVOc₈-OC₈ (100:20) *versus* PVK/Alq (60 nm) by their integration areas in Figure 8(a). According to aforementioned evidence, BVOc₈-OC₈ is confirmed to play a major role of emitting light in most of our devices. In addition, similar theoretical EL emission curves of PVK:BVOc₈-OC₈ as Alq = 20 and 40 nm shown in Figure 8(b) are acquired from the EL spectrum of PVK:BVOc₈-OC₈ (100:20)/Alq (20 nm) minus that of PVK/Alq (20 nm), and the EL spectrum of PVK:BVOc₈-OC₈ (100:20)/Alq (40 nm) minus that of PVK/Alq (40 nm), respectively. In comparison with previous results, a real EL emission curve of PVK:BVOc₈-OC₈ device without Alq is also measured and demonstrated in Figure 8(b). Interestingly, the theoretical EL emission curve of PVK:BVOc₈-OC₈ as Alq = 20 nm is most matched with the real EL emission curve of PVK:BVOc₈-OC₈ device without Alq. Thus, the mismatch of theoretical EL emission curves of PVK:BVOc₈-OC₈ as Alq = 40 and 60 nm may be due to the excimer emissions of BVOc₈-OC₈ emitters or the enhanced Alq emission by the hole transporting effect of BVOc₈-OC₈ in devices

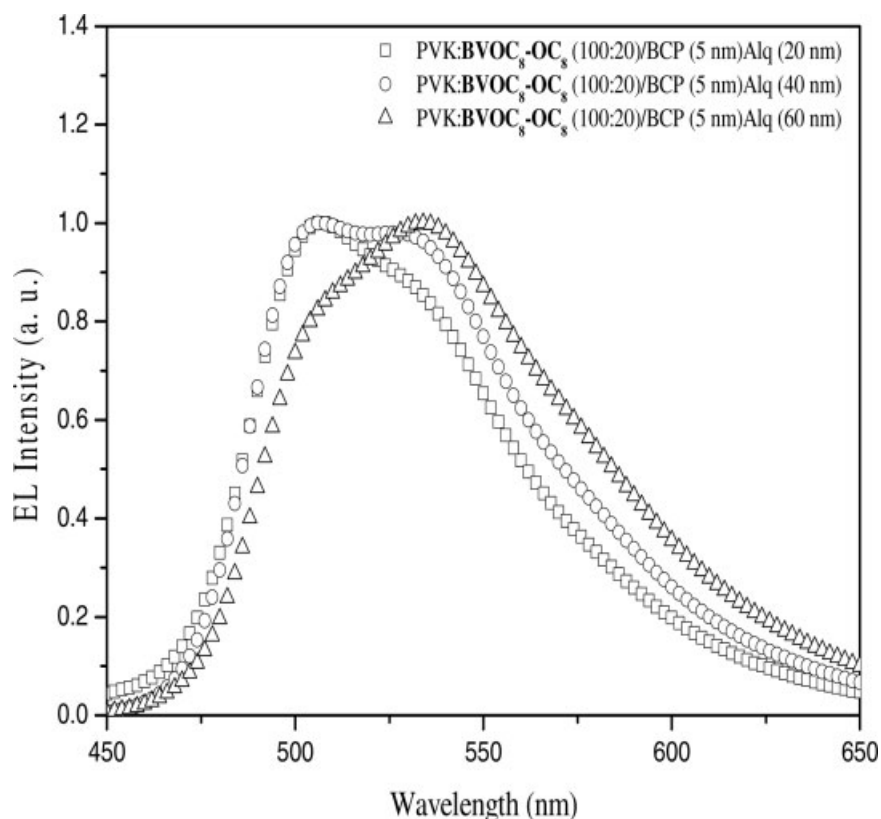


Figure 9. The EL characteristics of PVK:BVOC₈-OC₈ (100:20)/BCP (5 nm)/Alq (X nm) devices with different thicknesses of ETL (Alq), that is X = 20, 40, and 60 nm.

of PVK:BVOC₈-OC₈ (100:20)/Alq (40 nm) and /Alq (60 nm). Conclusively, the EL spectra of PVK:BVOC₈-OC₈ (100:20)/TPBI (60 nm) (in Fig. 6) and PVK:BVOC₈-OC₈ (100:20)/Alq (20 nm) (in Fig. 7) are quite similar to that of PVK:BVOC₈-OC₈ (100:20) without ETL [shown in Fig. 8(b)], and so the EL emissions of these results are originated from the conjugated emissions of BVOC₈-OC₈ emitters.

Since Alq is proved not to be a main luminescent ingredient, BVOC₈-OC₈ plays a more important role in EL. Thus, one layer of hole-blocking BCP is added between the emitting layer and Alq (ETL) to evaluate the role of ETL and the emission mechanism. In principle, Alq emits partial light in the device without hole-blocking layer of BCP (or with 5 nm of BCP), the main light-emission may come from the layer of PVK:BVOC₈-OC₈ (100:20). By increasing the thickness of BCP (from 0 and 5 nm to 10 nm) in [PVK:BVOC₈-OC₈ (100:20)/BCP/Alq] devices, the EL emission intensity of Alq relative to that of the chromophore should decrease. The decrease in the relative Alq emission (10 nm of BCP) originates from the reduction of electron and hole recombination in

Alq and the emitting light may be confined within the emitting layer of PVK:BVOC₈-OC₈. To confirm and eliminate the light emission of Alq, different thicknesses (5 and 10 nm) of BCP (hole-blocking layer) are added between an emitting layer (60 nm) of PVK:BVOC₈-OC₈ (100:20) and an ETL of Alq (20, 40, and 60 nm), which will result in less green emission of Alq. Usually, addition of a BCP layer causes a higher Q_{ext} efficiency but a higher turn-on voltage. However, hole-blocking BCP attached to PVK layer in this case induces a serious decay in EL and Q_{ext} efficiency, which may be due to the large variations of HOMO and LUMO energy levels between BCP and PVK. By increasing the thicknesses (from 5 to 10 nm) of BCP (hole-blocking layer), the turn-on voltage is increased and the maximum brightness is reduced, but the Q_{ext} efficiency is about the same. For instance, the turn-on voltage, the maximum luminescence (EL), and efficiency of previous devices are 3.2 V, 9978 cd/m², and 0.34% for PVK:BVOC₈-OC₈ (100:20)/BCP (5 nm)/Alq (40 nm) and 3.5 V, 6943 cd/m², and 0.35% for PVK:BVOC₈-OC₈ (100:20)/BCP (10 nm)/Alq (40 nm). No matter what is the thickness of BCP,

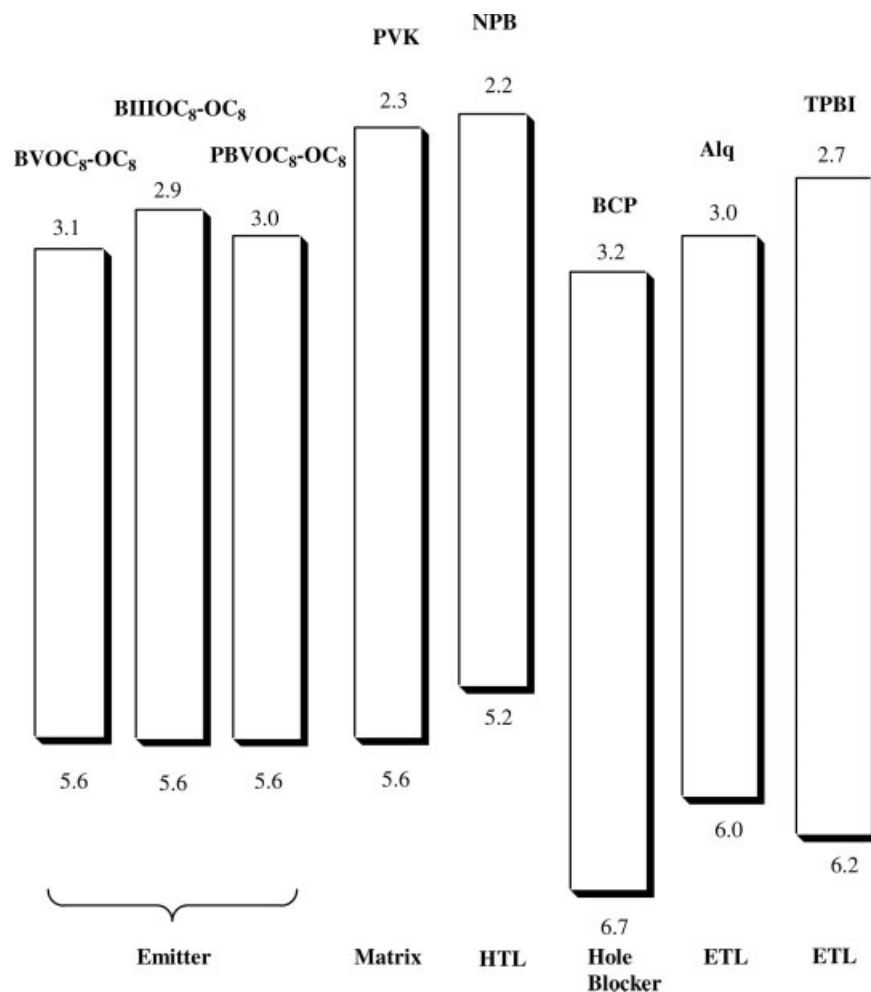


Figure 10. LUMO and HOMO energy values of various materials used in the PLED devices.

the EL emission λ_{\max} values (shown in Fig. 9) are red-shifted from 506 (as Alq = 20 and 40 nm) to 534 nm (as Alq = 60 nm) in the devices of PVK:BVOC₈-OC₈ (100:20)/BCP (5 nm)/Alq (*X* nm), which is similar to those devices without BCP, that is PVK:BVOC₈-OC₈ (100:20)/Alq (*X* nm). If the hole-blocking layer of BCP does work, the EL emission λ_{\max} values should not shift by increasing the thickness of ETL (Alq), or the EL emission λ_{\max} values should shift by increasing the thickness of BCP. Therefore, it is confirmed that the hole-blocking layer of BCP did not function well in these devices.

As for devices without hole-blocking layer of BCP, the thicknesses of Alq are adjusted to be 20, 40, and 60 nm (see Table 4). When the thickness of Alq is 20 nm, the maximum luminescence (EL), turn-on voltage, and efficiency of the device are (39,584 cd/m², 2.8 V, and 0.91%), where the electrons can go through Alq and reach PVK layer

completely. When the thickness of Alq is 60 nm, the corresponding EL properties of the device are (56,935 cd/m², 3.1 V, and 2.44%). The brightness of the latter device (60 nm Alq) is comparably larger than that of the former device (20 nm Alq), which is due to the light emission of the latter device (60 nm Alq) originated from both of the Alq layer and the interface between PVK:BVOC₈-OC₈ (100:20) and Alq. This can be explained by the LUMO and HOMO energy levels of device materials, which are shown in Figure 10. For example, (2.3, 5.6 eV) for PVK, (3.1, 5.6 eV) for BVOC₈-OC₈, (3.0, 6.0 eV) for Alq, and (3.2, 6.7 eV) for BCP, respectively. The LUMO values of BVOC₈-OC₈ (3.1 eV) and Alq (3.0 eV) are almost the same to make the electrons have equivalent possibility to stay at Alq and BVOC₈-OC₈ layers.

The EL characteristics of PVK:chromophore (100:5)/TPBI devices with emitting three-conjugated ring (BIII) and polymer (PBVOC₈) deriva-

Table 6. EL Characteristics of PVK:Chromophore (100:5)/TPBI Devices^a with BIII Derivatives and ETL (40 nm) of TPBI

	BIII-OMe	BIIIOMe-Me	BIIIOMe-OMe	BIIIOC ₈ -OMe	BIIIOC ₁₂ -OMe	BIIIOC ₈ -OC ₈
Turn-on voltage (V)	3.7	5.7	4.1	4.1	4.5	5.0
Max. brightness (cd/m ²)	5,862	5,320	2,794	6,050	5,908	5,774
Max. external quantum eff. (%)	1.10	0.97	0.72	0.83	0.67	0.61
Max. power eff. (lm/W)	0.59	0.43	0.19	0.34	0.22	0.19
λ_{\max} (FWHM) (nm)	468 (88)	462 (78)	462 (80)	466 (92)	470 (100)	466 (78)
CIE (x,y)	0.16,0.20	0.15,0.17	0.15,0.19	0.16,0.21	0.16,0.20	0.16,0.19
Voltage at 100 mA/cm ² (V)	10.9	11.5	15.2	13.7	13.2	13.0
Brightness at 100 mA/cm ² (cd/m ²)	1,410	1,076	928	1,012	898	805
External quantum eff. at 100 mA/cm ² (%)	0.99	0.88	0.72	0.74	0.67	0.61
Power eff. at 100 mA/cm ² (lm/W)	0.41	0.30	0.19	0.23	0.22	0.19

^a The thickness of TPBI is 40 nm and PVK:chromophore =100:5.

tives are shown in Tables 6 and 7, where the best ratio of PVK:chromophore possessing the brightest EL is 100:5 along with an ETL (40 nm) of TPBI. Compared with five-conjugated ring derivatives, three-conjugated ring derivatives possess lower densities of electron and larger energy gaps, thus to have blue shift of λ_{\max} values in PL and EL spectra (see Table 6). The band gaps of three-conjugated ring derivatives are about 2.7 eV and their PL and EL spectra all show blue light emissions. The smaller band gaps are due to the longer conjugation lengths of five-conjugated rings and their band gaps are about 2.5 eV to show greenish-blue light. Because an ETL of Alq

will emit green light from Alq, the ETL of Alq is replaced with TPBI to eliminate the additive emitting properties occurred in Alq (as no multiple light happens in devices with ETL of TPBI). BIIIOC₈-OMe is the brightest (EL) compound among these three-conjugated ring oligomers, possessing (6050 cd/m², 4.1 V, and 0.83%) for (the maximum EL, turn-on voltage, and $Q_{\text{ext.}}$ efficiency) in the device of PVK:chromophore/TPBI (shown in Table 6). Because five-conjugated ring polymers have similar conjugation lengths as the five-conjugated ring oligomers, their PL and EL spectra are alike because of their comparable energy band gaps. In polymer systems, PBVOC₈-

Table 7. EL Characteristics of PVK:Chromophore (100:5)/TPBI Devices^a with PBVOC₈-R₅ Derivatives and ETL (40 nm) of TPBI

	PBVOC ₈ -OC ₄	PBVOC ₈ -OC ₈	PBVOC ₈ -OC ₁₂	PBVOC ₈ -OEh
Turn-on voltage (V)	4.9	3.8	3.7	5.0
Max. brightness (cd/m ²)	3,953	3,778	2,908	6,972
Max. external quantum eff. (%)	0.67	0.58	0.71	0.75
Max. power eff. (lm/W)	0.29	0.35	0.29	0.44
λ_{\max} (FWHM) (nm)	500 (138)	498 (104)	492 (168)	498 (74)
CIE (x,y)	0.19,0.34	0.21,0.36	0.19,0.28	0.20,0.33
Voltage at 100 mA/cm ² (V)	17.6	14.6	15.6	12.9
Brightness at 100 mA/cm ² (cd/m ²)	986	962	841	1,020
External quantum eff. at 100 mA/cm ² (%)	0.50	0.45	0.51	0.54
Power eff. At 100 mA/cm ² (lm/W)	0.18	0.21	0.17	0.25

^a The thickness of TPBI is 40 nm and PVK:chromophore =100:5.

OEh is the brightest (EL) compound among these polymer derivatives, which possesses EL characteristics of (6972 cd/m², 5.0 V, and 0.75%) shown in Table 7. PBVOC₈-OEh has the smallest FWHM value (74 nm) of EL spectra among PBVOC₈ polymer derivatives because it has the narrowest distribution of energy gaps in PVK. In general, three-conjugated ring BIII derivatives and polymer derivatives (PBV) have worse EL properties, for example, maximum EL, turn-on voltage, and Q_{ext} efficiency, than five-conjugated ring BV derivatives.

CONCLUSIONS

Highly efficient green EL emissions of PVK PLED devices doped with fluorescent oligo(*p*-phenylene-vinylene)s (BIII and BV) and polymer derivatives (PBV) were obtained by proper device configurations of multilayer design. BVOC₈-OC₈ is the brightest (EL) emitter among all chromophores used in this study. The brightest device PVK: BVOC₈-OC₈(100:20)/Alq (60 nm/60 nm) has a brightness of 56,935 cd/m² with a power efficiency of 3.25 lm/W. It suggests that the emission mechanism (including the conjugated and excimer emissions of BVOC₈-OC₈ emitters as well as Alq emissions) originate from both of BVOC₈-OC₈ and ETL (Alq) by varying the concentration of chromophores and adjusting the thickness of ETL. The excimer emissions of BVOC₈-OC₈ emitters are affected by the concentration of the emitters (i.e. PVK:BVOC₈-OC₈ = 100:20 is the best concentration among our study), the thickness, and the type (different effect for Alq and TPBI) of ETL. Five-conjugated ring OPV (BV) derivatives with proper alkoxy groups possess excellent hole-transporting property and the highest brightness in PLED devices, and the main emitting source of these multilayer devices is confirmed to be the conjugated emissions and excimer emissions of the OPV emitters.

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