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Blue Emitting Polymers as Host Materials of Phosphorescent Dopant and Their Electroluminescent Properties

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Two types of blue electroluminescent conjugated polymers, poly(BP-alt-BCV) and poly(BFMP12-BPV), were prepared by Horner-Emmons polycondensation and used as host polymers for the phosphorescent dopant, (bsn)₂Ir(acac). Poly(N-vinylcarbazole) (PVK), known as a blue emitting material, was also used for comparison with these polymers. Electrophosphorescence of PLEDs with these dopant/host systems was investigated in terms of luminescence, efficiency, emission color, and energy transfer. The poly(BP-alt-BCV) showed blue emission of high color purity ($x = 0.18$, $y = 0.19$), however, poly(BP-alt-BCV) host/phosphorescent (bsn)₂Ir(acac) dopant showed red emission ($x = 0.60$, $y = 0.37$) due to an efficient energy transfer from poly(BP-alt-BCV) host polymer to phosphorescent (bsn)₂Ir(acac) dopant.

Keywords: blue emitting host polymer; phosphorescent dopant; phosphorescent organic light emitting diode (PhOLED); polymer light emitting diode (PLED)

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INTRODUCTION

Conjugated polymers are especially useful in polymer light emitting diodes (PLEDs) since they could readily be incorporated in LEDs by simple spin-coating or ink-jet printing method. Because of these advantages it is envisaged that PLEDs may provide the platform for the next generation of displays [1,2]. However, recent research in organic light emitting diodes (OLEDs) has focused on the synthesis and evaluation of new phosphorescent materials in an effort to improve EL efficiencies. These phosphorescent materials have been utilized as dopants both in the OLEDs and PLEDs for the purpose of improving quantum efficiency and color tuning. In case of OLEDs using low molecular weight emitting materials, each organic layer is generally fabricated by vacuum deposition method. However, this method is cost ineffective and the performance of OLEDs was greatly affected by thermal properties of organic materials and deposition conditions employed.

In this work, blue emitting conjugated copolymers were synthesized by using Horner-Emmons polycondensation as a candidate for host material of phosphorescent dopant for the purpose of utilizing spin coating process instead of vacuum deposition. Emission properties of PLEDs fabricated with these polymers doped with phosphorescent $(\text{bsn})_2\text{Ir}(\text{acac})$ were evaluated. It has been reported [3] that 4,4'-*N,N'*-dicarbazole biphenyl (CBP) containing both carbazole group and biphenyl moiety was widely used as a host material in phosphorescent organic light emitting diodes (PhOLEDs). Therefore, a new electroluminescent polymer, poly(BP-*alt*-BCV), structurally similar to CBP, were synthesized as a host material for PhOLEDs. Poly(*N*-vinyl carbazole), PVK, and poly(BFMP12-BPV) containing a carbazole and a biphenyl moiety, respectively, were also investigated for comparison.

EXPERIMENTAL

Materials

2-Ethylhexylbromide (95%), 4-bromo-2,6-dimethylphenol (99.5+%), potassium *tert*-butoxide (95%), triethylphosphite (99%), copper iodide (98%), trans-1,2-cyclohexanediamine (99%), *N*-bromosuccinimide (99%), 4,4-bis(chloromethyl)-1,1'-biphenyl (95%), sodium ethoxide (96%), 2-nitropropane (97%), 1-naphthoic acid, 2-aminothiophenol, sodium hexachloroiridate(III) hydrate, 2,4-pentandione and 1,12-dibromododecane were purchased from Aldrich Chemical Co.. Reagent grade carbazole,

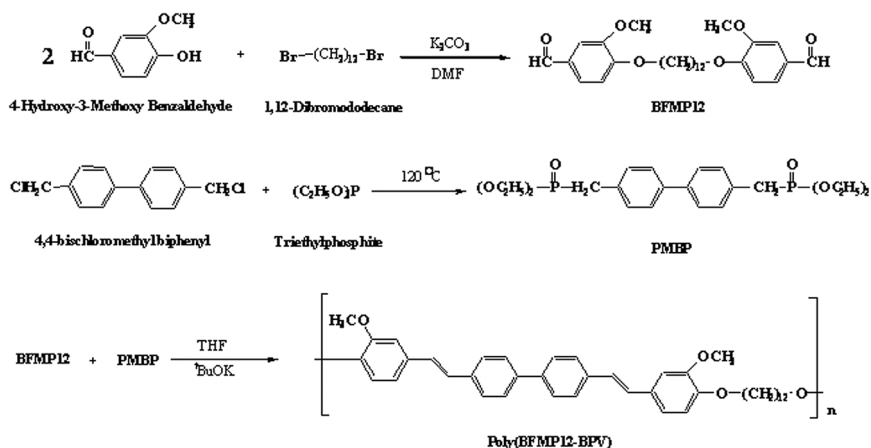
n-dodecane, benzoyl peroxide, phosphoric acid and 4-hydroxy-3-methoxy benzaldehyde were obtained from Tokyo Kasei Co. and used as received. Solvents were reagent grades and purified prior to use. Tris(8-hydroxyquinolino)aluminum (Alq₃) was obtained from Tokyo Kasei Co. and used as received. Indium-tin oxide (ITO) coated glass with a sheet resistance of 30 Ω/□ was obtained from Samsung Corning Co. Aluminum (99.99%, CERAC, USA) was used to deposit anode electrode. PVK (M_n = 48,800; M_w/M_n = 1.68) used as a host material was purchased from Aldrich Chemical Co.

Synthesis of Poly(BFMP12-BPV)

The synthetic scheme to poly(BFMP12-BPV) is shown in Scheme 1.

1,12-Bis(4-formyl-2-methoxyphenoxy)dodecane (BFMP12)

4-Hydroxy-3-methoxybenzaldehyde (7.61 g, 0.05 mol), potassium carbonate (8.29 g, 0.06 mol) and 1,12-dibromododecane (8.20 g, 0.025 mol) were dissolved in 200 mL of DMF and refluxed for 12 h [4,5]. DMF was removed using vacuum and the remaining mixture was extracted several times with water and dichloromethane. After evaporating dichloromethane, the product was precipitated by adding excess amount of water and recovered by filtration. The reaction product 1,12-bis(4-formyl-2-methoxyphenoxy)dodecane, BFMP12, was recrystallized from methanol.



SCHEME 1 Synthetic route to poly(BFMP12-BPV).

Yield: 64%, $^1\text{H-NMR}(\text{CDCl}_3)$, δ : 9.85 (s, 2H, $-\text{CHO}$), 7.43 (q, 4H, aromatic H in meta and para to $-\text{OCH}_3$), 6.96 (d, 2H, aromatic H in ortho to $-\text{OCH}_3$), 4.10 (t, 4H, $-\text{OCH}_2-$), 3.93 (s, 6H, $-\text{OCH}_3$), 1.88, 1.42 (m, 20H, $-(\text{CH}_2)_{10}-$), IR(KBr), cm^{-1} : 3075 (Ar CH), 2926 (aliphatic CH), 2762 (aldehydic hydrogen), 1677 (C=O), 1586, 1510 (Ar C=C), 1263 (Ar-O-C).

4,4'-Bis(diethoxyphosphinylmethyl)-1,1'-biphenyl (PMBP)

Phosphonate was synthesized using Arbuzov reaction [7,8]. Mixture of triethylphosphite (20 g, 0.12 mol) and 4,4-bischloromethyl biphenyl (2.62 g, 0.01 mol) was stirred at 120°C for 12 h. Unreacted triethylphosphite was removed under reduced pressure after cooling down to room temperature. After dissolving the reaction product in ethanol, unreacted 4,4-bischloromethyl biphenyl was removed by filtration. The product, PMBP, was obtained by removing ethanol under reduced pressure and then vacuum drying.

Yield: 88%, $^1\text{H-NMR}(\text{CDCl}_3)$, δ : 7.52, 7.36 (m, 8H, Ar-H), 4.04 (m, 8H, P-OCH₂-), 3.20 (d, 4H, Ar-CH₂P), 1.27 (t, 12H, -CH₃), IR(KBr), cm^{-1} : 3030 (Ar CH), 2987 (aliphatic CH), 1238 (P=O).

Poly(BFMP12-BPV) [poly(1,12-dodecanedioxy-2-methoxy-1,4-phenylene-1,2-ethenylene-1,1'-biphenyl-4,4'-ylene-1,2-ethenylene-3-methoxy-1,4-phenylene)]

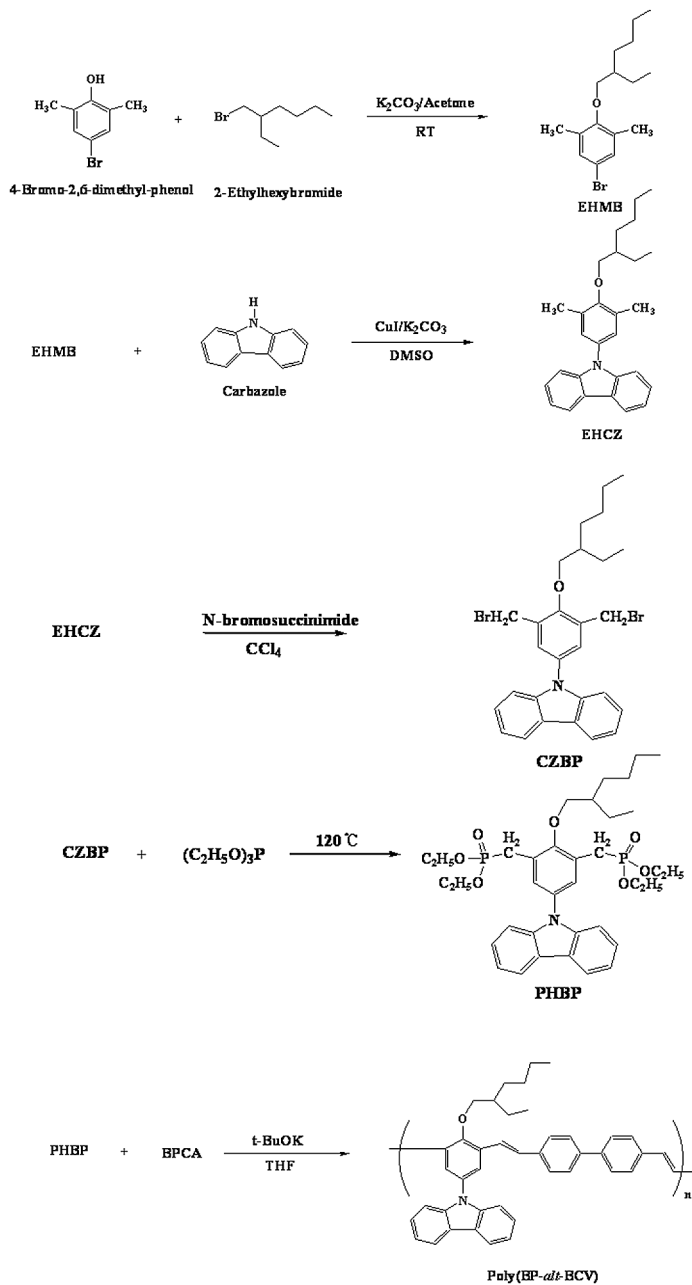
Poly(BFMP12-BPV) was prepared by using Honer-Emmons polycondensation [9–11]. BFMP12 (4.70 g, 0.01 mol) and PMBP (4.54 g, 0.01 mol) were dissolved in 100 mL of THF. The solution of tBuOK (4.73 g, 0.04 mol) in 80 mL of THF was added dropwise for 10 min. The reaction product was precipitated after 20 min and then stirred for 7 h. After evaporation of THF under reduced pressure, poly(BFMP12-BPV) was obtained by successive washing with water and methanol, followed by filtration. IR(KBr) of poly(BFMP12-BPV), cm^{-1} : 3021(Ar CH), 2931 (aliphatic CH), 1596, 1511 (Ar C=C), 1248 (Ar-O-C), 963 (trans vinylene).

Synthesis of Poly(BP-*alt*-BCV)

The synthetic scheme to the poly (BP-*alt*-BCV) is shown in Scheme 2.

5-Bromo-2-(2-ethylhexyloxy)-1,3-dimethyl-benzene (EHMB)

4-Bromo-2,6-dimethyl-phenol (0.02 mol) in 50 ml of acetone was added dropwise to a suspension of potassium hydroxide (0.06 mol) in 200 ml of acetone which was prepared by vigorous stirring for 30 min under nitrogen atmosphere. 2-Ethylhexyl bromide (0.02 mol) was



SCHEME 2 Synthetic route to poly(BP-*alt*-BCV).

added to the solution, followed by reflux for 48 h [12]. EHMB was obtained as liquid in 40% yield. $^1\text{H-NMR}$ (CDCl_3), δ : 7.15 (2H, Ar-H), 3.60 (2H, $-\text{O}-\text{CH}_2-$), 2.26 (6H, Ar CH_3), 2.18 (9H, $-\text{CH}-$, $-\text{CH}_2-$), 0.91 (6H, $-\text{CH}_3$).

9-[4-(2-Ethyl-hexyloxy)-3,5-dimethyl-phenyl]-9H-carbazole (EHCZ)

EHCZ was synthesized by using Ullmann reaction [13,14]. Copper iodide (3.2×10^{-4} mol) and carbazole (3.84×10^{-2} mol) were added to the solution of potassium carbonate (7.6×10^{-2} mol) in 50 ml of dioxane, and then temperature was increased over a time period of 1 h to 110°C while stirring. At 110°C , EHMB (3.2×10^{-2} mol), trans-1,2-cyclohexanediamine (3.2×10^{-3} mol) and n-dodecane (6.4×10^{-3} mol) was added and reacted for 24 h. EHCZ was obtained as liquid in 27.1% yield. $^1\text{H-NMR}$ (CDCl_3), δ : 7.38 (4H, Ar-H), 7.26 (4H, Ar-H), 7.16 (2H, Ar-H), 3.59 (2H, $-\text{O}-\text{CH}_2-$), 2.36 (6H, Ar- CH_3), 2.14 (9H, $-\text{CH}-$, $-\text{CH}_2-$), 0.95 (6H, $-\text{CH}_3$).

9-[3,5-Bis-bromomethyl-4-(2-ethyl-hexyloxy)-phenyl]-9H-carbazole (CZBP)

N-Bromosuccinimide (NBS) (1.74×10^{-2} mol) was added to the solution of EHCZ (8.7×10^{-3} mol) in 100 ml of carbon tetrachloride [15]. The reaction mixture was refluxed for 12 h after addition of benzoyl peroxide (6.6×10^{-5} mol). Unreacted NBS was removed from the resulting mixture by filtration. CZBP was obtained as liquid in 31% yield. $^1\text{H-NMR}$ (CDCl_3), δ : 7.48 (4H, Ar-H), 7.45 (4H, Ar-H), 7.35 (2H, Ar-H), 4.46 (4H, $-\text{CH}_2\text{Br}$), 3.96 (2H, $-\text{O}-\text{CH}_2-$), 2.25 (9H, $-\text{CH}-$, $-\text{CH}_2-$), 0.95 (6H, $-\text{CH}_3$).

[5-Carbazol-9-yl-3-(diethoxy-phosphorylmethyl)-2-(2-ethyl-hexyloxy)-benzyl]-phosphonic acid diethyl ester (PHBP)

PHBP was prepared using Arbuzov reaction of CZBP (5.4×10^{-3} mol) with triethylphosphite (0.108 mol) at 120°C for 12 h. PHBP was obtained as liquid in 68.5% yield. $^1\text{H-NMR}$ (CDCl_3), δ : 7.48 (4H, Ar-H), 7.38 (4H, Ar-H), 7.35 (2H, Ar-H), 5.29 (4H, Ar- CH_2-), 3.76 (2H, $-\text{O}-\text{CH}_2-$), 2.36 (9H, $-\text{CH}-$, $-\text{CH}_2-$), 0.99 (6H, $-\text{CH}_3$).

4,4'-Biphenyldicarboxaldehyde (BPCA)

4,4'-Bischloromethylbiphenyl (0.04 mol) was dissolved in 150 ml of DMSO under nitrogen atmosphere until the solution became homogeneous. Sodium ethoxide (0.06 mol) and 2-nitropropane (0.06 mol) in 60 ml of ethanol was added dropwise to the solution, and then reacted for 3 h at room temperature. BPCA was obtained in 78% yield by

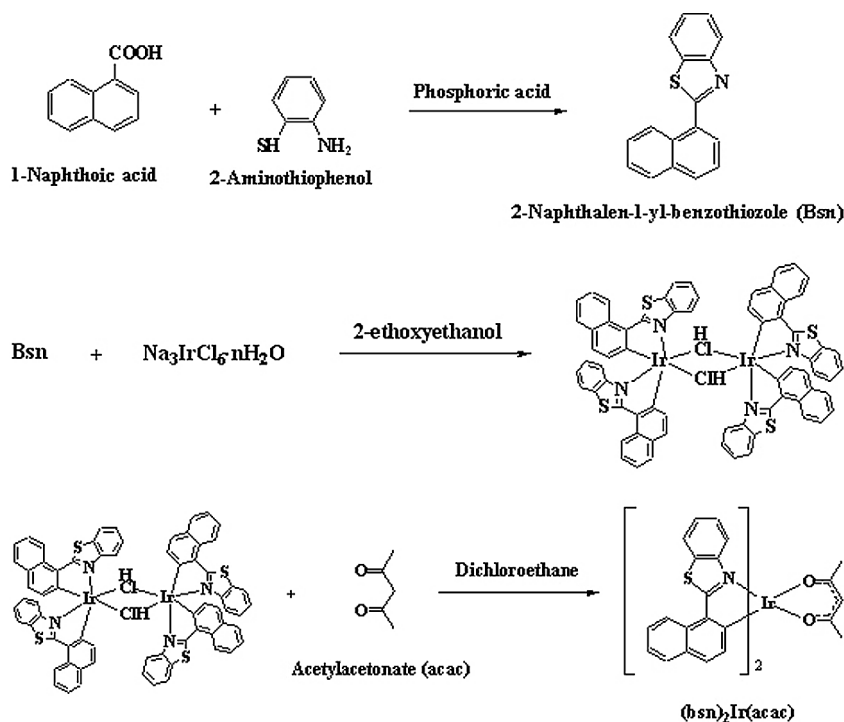
recrystallization from toluene. $^1\text{H-NMR}$ (CDCl_3), δ : 10.09 (2H, CHO), 7.7–8.01 (8H, Ar H).

Poly(BP-*alt*-BCV)

Poly(BP-*alt*-BCV) was prepared using Horner-Emmons polycondensation as presented in Scheme 2. Potassium *tert*-butoxide (0.29 mol) in 20 ml of THF was added dropwise over a time period of 10 min to PHBP (3.7×10^{-3} mol) and BPCA (3.7×10^{-3} mol) in 60 ml of THF. The reaction was carried out for 7 h at room temperature. Poly(BP-*alt*-BCV) was obtained in 52% yield.

Synthesis of $(\text{bsn})_2\text{Ir}(\text{acac})$

The synthetic route to red phosphorescent dopant [16] used in this study is seen in Scheme 3.



SCHEME 3 Synthetic route to $(\text{bsn})_2\text{Ir}(\text{acac})$.

2-Naphthalen-1-yl-benzothiozole (bsn)

1-Naphthoic acid (3 g, 0.017 mol) and 2-aminothiophenol (2.18 g, 0.017 mol) in 100 mL of phosphoric acid were refluxed with stirring for 12 h under N₂ atmosphere. After reaction distilled water was poured into the reaction medium to precipitate the product. The precipitate was filtered after neutralization with sodium bicarbonate. The filtrate was redissolved in methylene chloride and the product was recovered by evaporation of methylene chloride under reduced pressure. 2-Naphthalen-1-yl-benzothiozole (bsn) (1.02 g, 0.0039 mol) was obtained as liquid in 22.9% yield from column chromatography using n-hexane/ethylacetate = 9/1 as eluent. ¹H-NMR (CDCl₃): δ: 7.5–8.5 (m, aromatic H, 11H), Molecular weight Calcd. for C₁₇H₁₁NS: 261 Found: 261.

[(bsn)₂IrCl]₂

The solution of sodium hexa chloroiridate (III) hydrate (0.544 g, 0.0011 mol) and 2-naphthalen-1-yl-benzothiozole (bsn) (0.6 g, 0.0023 mol) in 100 mL of 2-ethoxyethanol was refluxed for 12 h under N₂ atmosphere. Distilled water was poured into the reaction medium to precipitate the product after cooling to room temperature. [(bsn)₂Ir(acac)]₂ (0.688 g, 0.00048 mol) was obtained in 21% yield by filtration, followed by washing with methanol several times. Molecular weight Calcd. for C₆₈H₄₂NSCl₂Ir: 1497 Found: 1497.

(bsn)₂Ir(acac)

The mixture of [(bsn)₂IrCl]₂ (0.5 g, 0.00033 mol), 2,4-pentandione (0.099 g, 0.00099 mol) and sodium carbonate (0.42 g, 0.00396 mol) in dichloroethane was stirred at 135°C for 1 h under N₂ atmosphere. After cooling to room temperature, the product was precipitated by addition of distilled water, followed by filtration. (bsn)₂Ir(acac) (0.235 g, 0.00029 mol) was obtained in 87.8% yield by washing with methanol several times. Molecular weight Calcd. for C₃₇H₂₉NSO₂: 812 Found: 812.

Fabrication of EL Devices

Doped and undoped double layer PLEDs were made by using poly(BP-*alt*-BCV), poly(BFMP12-BPV) and PVK as the host of emitting layer. Indium-tin oxide (ITO) coated glass was cut into 2.0 cm × 2.0 cm, and electrode area was prepared by photoetching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) solution. A solution (1 wt%)

of host polymer:(bsn)₂Ir(acac) (90:10 w:w) in tetrachloroethane (TCE) after filtration using MFS filter (0.45 μm pore size) was spin-coated on the ultrasonically cleaned ITO glass at 2500 rpm for 25 s and dried at 80°C for 1 h to give an emissive layer with a thickness of about 250–300 Å. After drying the emission layer the electron transporting Alq₃ layer was deposited with thermal evaporator. Al electrode was deposited at a rate of 20 Å/sec by thermal evaporation to give double layer [ITO/host polymer:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED.

Measurements

¹H-NMR spectra were taken on a Varian Unity Plus 300. Molecular weight and molecular weight distribution were measured by Waters gel permeation chromatography (GPC) equipped with Styragel HR 5E column using THF as an eluent against polystyrene standards at room temperature. UV-visible absorption spectra were obtained by Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). Electroluminescence (EL) spectra and color coordinates were measured by using Spectroscan PR 704 (Photoresearch Inc.). Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with Model 8092A Digital Multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100) equipped with close-up lens (No. 110, Φ 40.5 mm) at room temperature, respectively.

RESULTS AND DISCUSSION

Physical Properties of Conjugated Copolymers

The good solubility in common organic solvents at room temperature is one of the important properties of the synthesized copolymers for the fabrication of PLEDs by the simple spin casting method. It appeared that poly(BFMP12-BPV) was rarely soluble in NMP and tetrachloroethane (TCE) at 50°C. However, poly(BP-*alt*-BCV) showed high solubility at room temperature in common organic solvents such as THF, dichloroethane and TCE. The molecular weight of poly(BP-*alt*-BCV) was measured to be Mw = 13,080 g/mol (Mw/Mn = 1.34). On the other hand, the molecular weight of poly(BFMP12-BPV) could not be measured due to low solubility in THF. From TGA measurement, it was observed under N₂ atmosphere that decomposition temperatures of poly(BFMP12-BPV) and poly(BP-*alt*-BCV) were measured to be 396°C and 480°C, respectively.

UV-Vis and PL Properties of Conjugated Copolymers

UV-visible absorption and photoluminescence (PL) spectra of PVK, poly(BFMP12-BPV), poly(BP-*alt*-BCV) and phosphorescent dopant (bsn)₂Ir(acac) are presented in Figure 1. The photo-optical data are summarized in Table 1 in terms of UV-vis absorption maximum

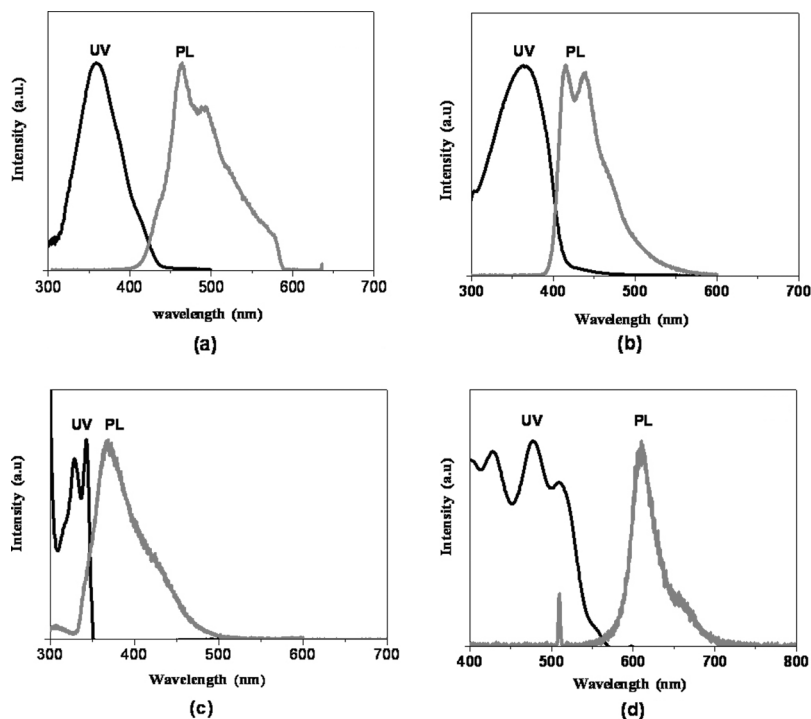


FIGURE 1 UV-visible absorption and photoluminescence spectra of (a) poly (BFMP12-BPV), (b) poly(BP-*alt*-BCV), (c) PVK and (d) (bsn)₂Ir(acac) solution in dichloroethane.

TABLE 1 Optical Properties of Host Polymers and Phosphorescent Dopant

Materials	$\lambda_{\max,UV}$ (nm/eV)	$\lambda_{\text{edg},UV}$ (nm/eV)	$\lambda_{\max,PL}$ (nm/eV)	Stoke's shift (nm)
Poly(BFMP12-BPV)	360/3.45	437/2.84	466/2.66	106
Poly(BP- <i>alt</i> -BCV)	365/3.40	414/3.00	406/3.05	41
PVK	343/3.62	351/3.53	370/3.35	27
(bsn) ₂ Ir(acac)	478/2.59	564/2.20	612/2.03	134

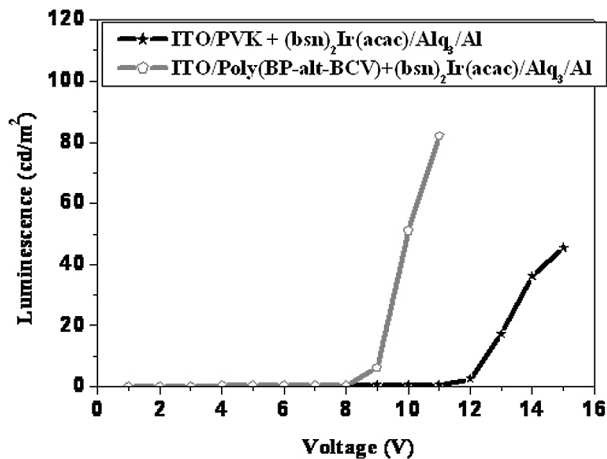
(maximum π - π^* transition, $\lambda_{\max,UV}$), band gap energy calculated from the absorption edge ($\lambda_{\text{edg},UV}$) [17], PL maximum ($\lambda_{\max,PL}$) and Stoke's shift [18,19]. It has been generally accepted that host matrix polymers have relatively high band gap energy, exhibiting in blue emission. All three host polymers showed $\lambda_{\max,PL}$ values in the range of blue emission, when excited at its own $\lambda_{\max,UV}$.

Electroluminescent Properties

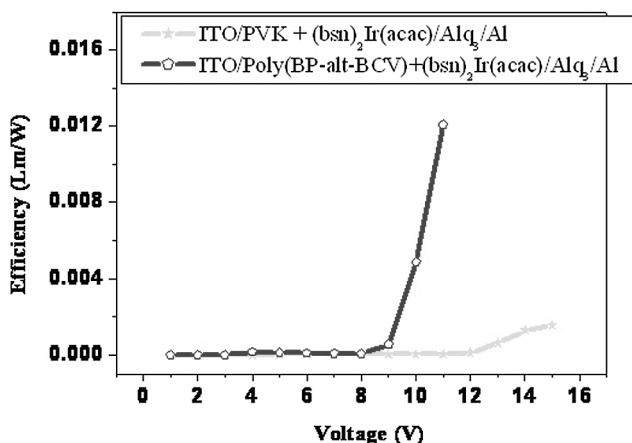
EL emission color of host polymers employed in this study was measured using undoped PLEDs such as [ITO/poly(BFMP12-BPV)/Alq₃/Al], [ITO/poly(BP-*alt*-BCV)/Alq₃/Al] and [ITO/PVK/Alq₃/Al] PLEDs. [ITO/poly(BFMP12-BPV)/Alq₃/Al] PLED exhibited low luminance and short lifetime, due to easy crystallization of poly(BFMP12-BPV) during device operation. Therefore, poly(BFMP12-BPV) was not further exploited as host material in this study. However, [ITO/poly(BP-*alt*-BCV)/Alq₃/Al] PLED exhibited 38 cd/m² of luminance at 13 V and blue emission ($x = 0.18$, $y = 0.19$ of CIE (Commission Internationale de l'Eclairage) coordinates). [ITO/PVK/Alq₃/Al] PLED showed blue emission ($x = 0.19$, $y = 0.19$), but lower luminance was observed than that of [ITO/poly(BP-*alt*-BCV)/Alq₃/Al].

Two types of doped PLEDs such as [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] and [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] were fabricated and their electroluminescent properties were evaluated. The maximum luminance and efficiency of doped [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED and [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED were presented in Figure 2. The maximum luminance and efficiency of doped [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED were measured to be 82 cd/m² (11 V) and 0.012 lm/W (11 V), while those of [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED were observed to be 45 cd/m² (15 V) and 0.0015 lm/W (15 V), respectively. It was considered from the above data that PLED with (bsn)₂Ir(acac)/poly(BP-*alt*-BCV) dopant/host system exhibited better EL properties than that with (bsn)₂Ir(acac)/PVK system. This result might be originated from structural similarity of poly(BP-*alt*-BCV) with CBP, both containing carbazole and biphenyl groups, resulting in better energy transfer than PVK which has only carbazole moiety in the repeat units. It has been reported that CBP with two carbazole rings connected by biphenyl group exhibited good host material property in the low molecular weight phosphorescent dopant/host system.

Figure 3 presents EL spectra measured from [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED and [ITO/PVK:(bsn)₂



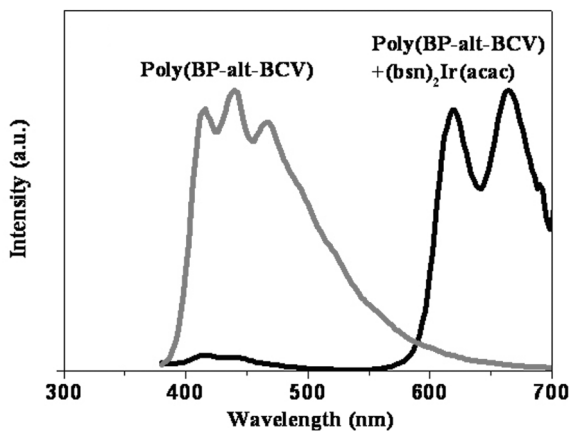
(a)



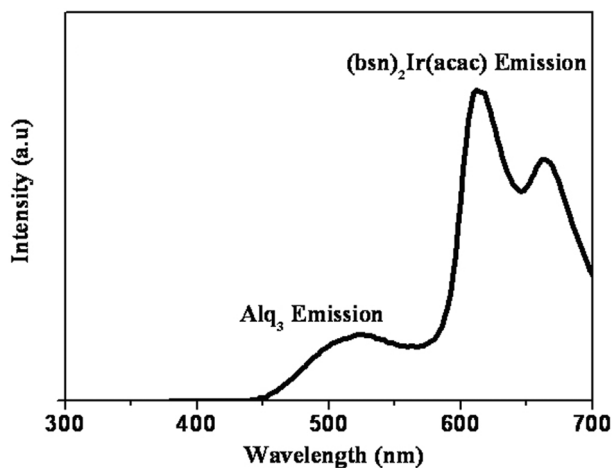
(b)

FIGURE 2 Luminance (a) and Efficiency (b) of PLEDs with voltage.

Ir(acac)(90:10 w:w)/Alq₃/Al] PLED. As seen in Figure 3(a), $\lambda_{\max,EL}$ of [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED were measured at 620 nm and 665 nm in the range of red emission, compared to blue emission ($\lambda_{\max,EL} = 440$ nm) of undoped [ITO/poly(BP-*alt*-BCV)/Alq₃/Al] PLED. This implies that electrons and holes injected from cathode and anode through poly(BP-*alt*-BCV) layer were effectively transferred to (bsn)₂Ir(acac) dopants, followed by the red emission from the excitons formed in (bsn)₂Ir(acac) dopants. A weak



(a)



(b)

FIGURE 3 EL emission spectra of (a) [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac) (90:10 w:w)/Alq₃/Al] PLED and (b) [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED.

blue emission seen in [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac) (90:10 w:w)/Alq₃/Al] PLED may be due to fluorescent poly(BP-*alt*-BCV), suggesting insufficient amount of dopants in emissive layer. It is therefore necessary to have balanced amount of dopants for the full red emission of (bsn)₂Ir(acac). As presented in Figure 3(b), [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED exhibited red emission from (bsn)₂

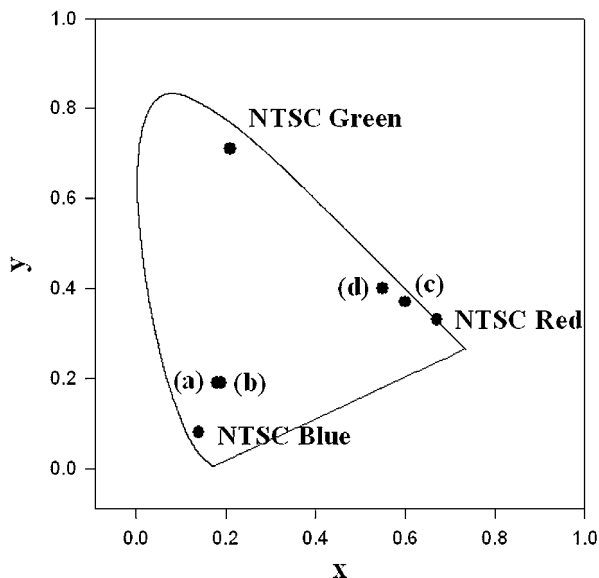


FIGURE 4 Color coordinates of (a) [ITO/poly(BP-*alt*-BCV)/Alq₃/Al] PLED, (b) [ITO/PVK/Alq₃/Al] PLED, (c) [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac) (90:10 w:w)/Alq₃/Al] PLED and (d) [ITO/PVK:(bsn)₂Ir(acac) (90:10 w:w)/Alq₃/Al] PLED in CIE 1931 chromaticity diagram [21].

Ir(acac) dopant as well as green emission from Alq₃ layer. It was found that the thickness of Alq₃ layer could be adjusted to get pure red emission from (bsn)₂Ir(acac) dopant.

EL emission colors of undoped [ITO/poly(BP-*alt*-BCV)/Alq₃/Al] and [ITO/PVK/Alq₃/Al] as well as doped [ITO/poly(BP-*alt*-BCV):(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] and [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLEDs are shown in Figure 4, according to NTSC chromaticity diagram [20]. It appeared that doped PLEDs exhibited red emission, while undoped PLEDs showed blue emission. It was also observed that [ITO/PVK:(bsn)₂Ir(acac)(90:10 w:w)/Alq₃/Al] PLED showed low color purity due to green emission from Alq₃ layer. This result may indicate that aromatic amine containing poly(N-vinyl carbazole), PVK, has better hole transport property than poly(BP-*alt*-BCV).

CONCLUSIONS

Synthesis of conjugated polymers, poly(BP-*alt*-BCV) and poly(BFMP12-BPV), was carried out by using Hornor-Emmons polycondensation. These conjugated polymers were used as host polymers

for the phosphorescent dopant, $(\text{bsn})_2\text{Ir}(\text{acac})$. Poly(*N*-vinylcarbazole) (PVK), known as a blue emitting material, was also used for comparison with these polymers. It was also found that while undoped [ITO/poly(BP-*alt*-BCV)/Alq₃/Al] PLED showed blue emission of high color purity ($x = 0.18$, $y = 0.19$), doped [ITO/poly(BP-*alt*-BCV): $(\text{bsn})_2\text{Ir}(\text{acac})(90:10 \text{ w:w})$ /Alq₃/Al] PLED exhibited red emission ($x = 0.60$, $y = 0.37$), implying efficient energy transfer from poly(BP-*alt*-BCV) host matrix to phosphorescent $(\text{bsn})_2\text{Ir}(\text{acac})$ dopant.

REFERENCES

- [1] Burn, P. L., Bradley, D. D. C., Friend, R. H., Halliday, D. A., Holmes, A. B., Jackson, R. W., & Kraft, A. (1992). *J. Chem. Soc.*, *1*, 3225.
- [2] Askari, S. H., Rughooputh, S. D., & Wudl, F. (1989). *Synth. Met.*, *29*, E129.
- [3] Watanabe, T., Nakamura, K., Kawami, S., Fukuda, Y., Tsuji, T., Wakimoto, T., Miyaguchi, S., Yahiro, M., Yang, M.-J., & Tsutsui, T. (2001). *Synthetic Metals*, *122*, 203.
- [4] Kim, Y., Kwon, S., Yoo, D., Rubner, M. F., & Wrighton, M. S. (1997). *Chem. Mater.*, *9*, 2699.
- [5] Gurge, R. M., Hickl, M., Krause, G., Lahti, P. M., Hu, B., Yang, Z., & Karasz, F. E. (1998). *Polym. Adv. Technol.*, *9*, 504.
- [6] Yang, Z., Sokolik, I., & Karasz, F. E. (1993). *Macromolecules*, *26*, 1188.
- [7] Paquette, L. A. (Ed.). (1995). *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons: New York, Vol. 7, 5082–5083, 5112–5116.
- [8] Larsen, M., Krebs, F. C., Jorgensen, M., & Harrit, N. (1998). *J. Org. Chem.*, *63*, 4420.
- [9] Mizuno, M., Fujii, K., & Tomioka, K. (1998). *Angew. Chem. Int. Ed.*, *37*, 515.
- [10] Rost, H., Teuschel, A., Pfeiffer, S., & Hörhold, H.-H. (1997). *Synth. Met.*, *84*, 269.
- [11] Cristau, H. J. & Taillefer, M. (1998). *Tetrahedron*, *54*, 1507.
- [12] Jung, E. S., Cho, E. H., & Chung, P. J. (1998). *J. of Korean Ind. & Eng. Chemistry*, *9*, 548.
- [13] Hassan, J., Seignion, M., Gozzi, C., Schulz, E., & Lemaire, M. (2002). *Chem. Rev.*, *102*, 1359–1469.
- [14] Klapars, A., Antilla, J. C., Huang, X., & Buchwald, S. L. (2001). *J. Am. Chem. Soc.*, *123*, 7727–7729.
- [15] Jin, S.-H., Jang, M.-S., & Suh, H.-S. (2002). *Chem. Mater.*, *14*, 643–650.
- [16] Lammansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H.-E., Adachi, C., Burrows, P. E., Forrest, S. R., & Thompson, M. E. (2001). *J. Am. Chem. Soc.*, *123*, 4304–4312.
- [17] Yamamoto, T., Yamada, W., Tagagi, M., Kizu, K., Maruyama, T., Ooba, N., Tomaru, S., Kurihara, T., Kaino, T., & Kubota, K. (1994). *Macromolecules*, *27*, 6620.
- [18] Suppan, P. (1994). *Chemistry and Light*, The Royal Society of Chemistry: Cambridge, 55–56.
- [19] Barashikov, N. N. & Gunder, O. A. (1994). *Fluorescent Polymers*, Ellis Horwood Ltd.: West Sussex, 177–187.
- [20] Ozawa, L. (1994). *Application of Cathodoluminescence to Display Devices*, Kodansha: Tokyo, 18–30.
- [21] MacAdam, D. L. (1981). Springer series in optical sciences. In: *Color Measurement; Theme and Variations*, MacAdam, D. L. (Ed.), Springer-Verlag: Berlin, Vol. 27, 17–25.