Synthesis and Characterization of Organic Light-Emitting Copolymers Containing Naphthalene

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Abstract: Conjugated PPV-derived block copolymers containing 2-ethylhexyloxynaphthalene unit were synthesized and characterized in this study. The resulting polymers were soluble in common organic solvents and showed good thermal stabilities. The weight-average molecular weights (M_w) of the copolymers ranged from 246,000 to 475,000 with PDIs of 1.3~2.1. The optical properties of these polymers, measured both in a chloroform solution and on a film, showed a maximum absorption at 405~476 nm for Copolymers I~VIII. In the PL spectra, Copolymers I~VIII showed maximum peaks at 510~566 nm. The HOMOs, LUMOs and band gaps of the PPV derivatives of Copolymers I~VIII were 5.30~5.77, 3.04~3.24, and 2.5~2.2 eV, respectively. The multi-layered, light-emitting diodes of ITO/PEDOT/copolymers/LiF/Al exhibited turn-on voltages of 6~2.5 V. Copolymer VIII exhibited the maximum brightness of 3,657 cd/m². Particularly, Copolymer VII, with an identical composition of MEH-PPV and naphthalene-PPV, showed a maximum luminance efficiency and power efficiency of 2.63 cd/A and 1.06 lm/W, respectively.

Keywords: PPV, naphthalene, energy transfer, OLED.

Introduction

Since the first demonstration of the electroluminescence (EL) of poly(*p*-phenylenevinylene) (PPV) by Holmes *et al.*, many different types of polymer light-emitting diodes (PLEDs) have been extensively reported.[1-8] They have been developed and applied due to remarkable advantages such as their self-emission, low operating voltage, color tunability, wide viewing angle, fast switching time, easy fabrication at low cost, and potential applications to full color flat panel displays and flexible displays.[9-15]

Despite their many advantages, there are several issues that must be resolved, such as the device lifetime and luminescence. These are related to imbalanced charge injection/transporting, excimer/exciplex or aggregate formation, and structural defects in the polymers that result from head-head and tail-tail linkage during Gilch polymerization.[15-23] These conditions lead to a low luminescent efficiency and short

lifetime of PPV-derived LEDs. To resolve the structural defects, the authors and other groups have investigated naphthyl-substituted poly(*p*-phenylenevinylene)s (N-PPVs);[15,24] it was found that the introduction of a bulky naphthyl side chain can cause the polymers to impose even great steric hindrance, which leads to negligible structural defects due to the asymmetric structure and the improved thermal stability with higher glass-transition temperatures. It also causes an increase in the solubility and prevents the generation of excimers due to molecular interaction.[15,22-34,36,37] Therefore, it creates a highly efficient material.
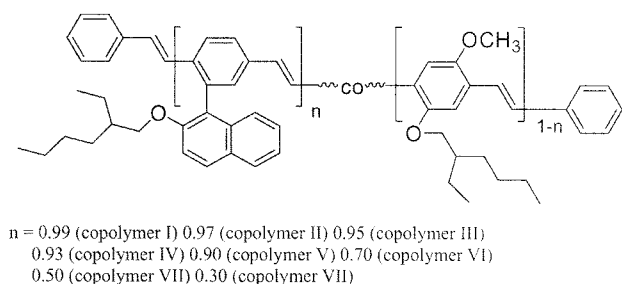
From a synthetic point of view, polymers offer the possibility of tuning their emission color and changing the energy position of the frontier levels, thereby allowing control of the charge injection barriers at polymer-electrode and polymer-polymer interfaces. A strategy to achieve this goal is the preparation of copolymers, combining highly luminescent moieties such as MEH-PPV moiety, and rigid bulky moieties while inhibiting intermolecular interactions.

In this paper, copolymers derived from MEH-PPV and naphthyl-substituted PPV (EHN-PPV) (Scheme I) were designed and synthesized. It is expected that the introduction of naphthyl side chain can give steric hindrance to

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Scheme I

n = 0.99 (copolymer I) 0.97 (copolymer II) 0.95 (copolymer III)
0.93 (copolymer IV) 0.90 (copolymer V) 0.70 (copolymer VI)
0.50 (copolymer VII) 0.30 (copolymer VII)

copolymer, which leads to decrease the defect and intermolecular interaction, and to increase the thermal stability with high T_g. Their photo physical, thermal and electrochemical properties were investigated in terms of changes in the composition of the copolymer. Additionally, the results of the EL devices fabricated from these new copolymers are reported.

Experimental

Materials. All reagents and solvents were purchased from Aldrich Chemical Co., Fluka and Lancaster. Only analytical-grade quality chemicals were used. PEDOT was purchased from Bayer. Spectroscopic-grade $CHCl_3$ (Aldrich) was used for all absorption and emission experiments.

Synthesis of 1-Bromo-2-(2-Ethylhexyloxy)Naphthalene. A mixture of 1-bromo-2-naphthol (25 g, 0.112 mol), 2-ethylhexyl bromide (32.4 g, 0.168 mol), KOH (7.54 g, 0.134 mol), and little amount of NaI was refluxed in ethanol (250 mL) for 15 h, after then it was removed ethanol and was added pure water. The reacted mixture was extracted with hexane and was removed solvent. The product was purified by column chromatography over silica gel using hexane as the product to give 30 g (80%). FT-IR (KBr) (cm⁻¹): 3054-3000 (aromatic C-H), 3000-2800 (aliphatic C-H), 1595, 1502, 1460 (C=C), 1271, 1243 (aromatic C-O), 1038 (aromatic C-Br), ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 8.24-8.27 (d, 1H), 7.95-7.78 (m, 2H), 7.6-7.55 (t, 1H), 7.43-7.38 (t, 1H), 7.29-7.26 (d, 1H), 4.13-4.05 (d, 2H), 1.91-1.83 (m, 1H), 1.71-1.49 (m, 4H), 1.45-1.31 (m, 4H), 1.03-0.91 (m, 6H).

Synthesis of 2-Bromo-*p*-Xylene. A solution of bromine (165.6 g, 1.036 mol) in some amount of dichloromethane was added slowly to a solution of *p*-xylene (100 g, 0.942 mol) in dichloromethane for 1 h at 0 °C. The mixture was allowed to warm to room temperature and stirred for 10 h after then it poured in ice and 10% aqueous sodium hydroxide (400 mL). And it was stirred for 2 h and was extracted with dichloromethane. The organic layer was removed solvent and vacuum distillated (50 °C/Torr). Yield: 98 g (56%), ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 7.43 (s, 1H), 7.17 (d, 1H), 7.07 (d, 1H), 2.42-2.36 (d, 6H), FT-IR (KBr) (cm⁻¹): 3021 (aromatic C-H), 1448, 1447, 1382 (C=C), 2976-2861 (aliphatic C-H), 1041 (aromatic C-Br).

Preparation of 1,4-Dimethylphenylboronic Acid. A solution of 2-bromo-*p*-xylene (20 g, 0.108 mol) in absolute diethyl ether was stirred and was allowed to cool to -78 °C. 2.5 M *n*-BuLi (65 mL, 0.162 mol) was added slowly to it. The mixture was warmed to room temperature and was stirred for 1 h. After then it was cooled to -78 °C and was added triethylborate (23.5 g, 0.162 mol). It was stirred for 12 h at room temperature and it was quenched in aqueous 2 N-HCl before was extracted with diethyl ether. The solvent was completely removed and was recrystallized in a solution of hexane: diethyl ether (6:4). Yield: 6 g (67%), m.p: 89~90 °C, ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 8.02-7.82 (t, 1H), 7.29-7.09 (m, 2H), 2.83-2.34 (m, 6H), FT-IR (KBr) (cm⁻¹): 3300 (-OH), 3031 (aromatic C-H), 2963, 2924, 2866 (aliphatic C-H), 1604-1493 (C=C).

Synthesis of 1-(2,5-Dimethylphenyl)-2-(2-Ethylhexyloxy)-Naphthalene. A mixture of 1-bromo-2-(2-ethyl-hexyloxy)-naphthalene (1) (8 g, 0.024 mol), 1,4-dimethylphenyl-boronic acid (3) (4.29 g, 0.028 mol) and a little 2 M-K₂CO₃ in THF (70 mL) was stirred for 30 min under nitrogen. After tetrakis (triphenylphospine)-palladium (0.3 g) was put into a mixture, and it was reacted for 12 h at 85~95 °C. And then the mixture was quenched in 2 N-HCl, before it was extracted with hexane. The solvent was completely removed and the solid was purified by column chromatography over silica gel using hexane. Yield: 7 g (88%), m.p: 191 °C, ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 7.91-7.84 (m, 2H), 7.42-7.17 (m, 6H), 6.99 (s, 1H), 3.94-3.91 (m, 2H), 2.37 (s, 3H), 1.94 (s, 3H), 1.56 (m, 1H), 1.30-1.19 (m, 8H), 0.89-0.79 (m, 6H), FT-IR (KBr) (cm⁻¹): 3050, 3015 (aromatic C-H), 2959-2864 (aliphatic C-H), 1620, 1591, 1504, 1461 (C=C), 1328, 1265, 1064 (aromatic C-O).

Synthesis of 1-(2,5-Bis(Bromomethyl)Phenyl)-2-(2-Ethyl-hexyloxy)-Naphthalene (EHNBMP). After 1-(2,5-dimethyl-phenyl)-2-(2-ethyl-hexyloxy)-naphthalene (11 g, 0.03 mol) was dissolved in benzene (100 mL), N-bromosuccinimide (NBS) (13.05 g, 0.07 mol) and BPO (1 g) were added to that and the mixture was refluxed for 2 h under nitrogen. The mixture was allowed to cool and was filtered succinimide before extracted with hexane. The organic layer was dried over anhydrous magnesium sulfate, filtered, and removed solvent completely. And it was purified by column chromatography over silica gel using hexane: ethyl acetate (100:1). Yield: 5.0 g (30%), ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 8.02-7.93 (m, 2H), 7.73-7.70 (d, 1H), 7.56-7.37 (m, 6H), 4.58 (s, 2H), 4.38 (s, 2H), 4.41-3.97 (m, 2H), 1.65 (s, 1H), 1.38-1.30 (m, 8H), 1.00-0.87 (m, 6H), FT-IR (KBr) (cm⁻¹): 3055, 3020 (aromatic C-H), 2957-2870 (aliphatic C-H), 1621, 1591, 1509, 1461 (C=C), 1332, 1275, 1225 (aromatic C-O), 650 (aliphatic C-Br).

Synthesis of 1-Methoxy-4-(2-Ethyl-Hexyloxy)Benzene. The procedure was followed by literature method and purification.[35] Yield: 236 g (82.6%), ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 6.88 (s, 4H), 3.85-3.78 (m, 5H), 1.75-1.69 (m, 1H),

1.57-1.28 (m, 8H), 0.96-0.90 (m, 6H), FT-IR (KBr) (cm⁻¹):
3049 (aromatic C-H), 2960, 2864 (aliphatic C-H), 1588,
1508, 1465 (C=C), 1290, 1233, 1041 (aromatic C-O).

Synthesis of 2,5-Bis(Chloromethyl)-1-Methoxy-4-(2-Ethylhexyloxy)-Benzene (MEHB). The procedure was
followed by literature method and purification.[35] Yield: 19 g
(67%), m.p: 55~58 °C, ¹H NMR (CDCl₃, 300 MHz) δ[ppm]:
6.94-6.93 (d, 2H), 4.65 (s, 4H), 3.93-3.85 (m, 5H), 1.63-
1.27 (m, 10H), 0.98-0.90 (m, 6H), FT-IR (KBr) (cm⁻¹): 3050
(aromatic C-H), 2957-2863 (aliphatic C-H), 1514, 1464
(C=C), 1315, 1264, 1222, 1033 (aromatic C-O), 734, 696,
608 (aliphatic C-Cl).

Synthesis of Copolymers. Copolymer 1 was synthesized
following procedure. A solution of potassium-*tert*-butoxide
(0.9 g, 7.68 mmol) in 1,4-dioxane (60 mL) was slowly
added to a deoxygenated mixture of monomer I (0.5 g,
0.965 mmol), monomer II (3.25 mg, 0.58 mmol) in amount
of 1,4-dioxane. It was stirred for 10 h at room temperature,
and a small quantity of chloromethyl-benzene was added to
a mixture and end-capped for 4 h at 60 °C. The mixture was
allowed to cool to room temperature, and was precipitated
with methanol. The solid was filtered and washed with 2 N-
HCl. And the solid was dissolved into chloroform and was
precipitated with methanol. After then it was filtered and
was dried in a vacuum oven. Yield: 0.25 g (70%), FT-IR
(KBr) (cm⁻¹): 3080-3010 (aromatic C-H), 2975-2840 (aliphatic C-H), 1860-1430 (C=C), 1321-1210, 1050-1010
(aromatic C-O).

Copolymer II~VIII were obtained by same method of
copolymer I.

Instrument. The ¹H NMR spectra were recorded with a
Bruker AM-200 spectrometer. The FT-IR spectra were measured on a Bomen Michelson series FT-IR spectrometer.
The melting points were determined with an Electrothermal
Mode 1307 digital analyzer. The thermal analysis were performed on a TA TGA 2100 thermogravimetric analyzer in a
nitrogen atmosphere at a rate of 20 °C/min. Differential
scanning calorimeter (DSC) was conducted under nitrogen
on a TA instrument 2100 DSC. The sample was heated with
20 °C/min from 30 to 250 °C. UV-vis absorption spectra and
photoluminescence spectra were measured by Perkin Elmer
LAMBDA-900 UV/VIS/IR spectrophotometer and LS-50B
luminescence spectrophotometer, respectively. The photoluminescence spectra were reacted on a Perkin-Elmer LS-50
fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Molecular weights and polydispersities of the copolymers were determined by gel permeation
chromatography (GPC) analysis with polystyrene standard
calibration (waters high-pressure GPC assembly Model
M515 pump, u-Styragel columns of HR4, HR4E, HR5E, with
500 and 100 Å, refractive index detectors, solvent THF).
Cyclic voltammetry (CV) was performed on an EG and G
Parc model 273 Å potentiostat/galvanostat system with a
three-electrode cell in a solution of Bu₄NBF₄ (0.1 M) in acetonitrile at a scan rate of 100 Mv/S. The polymer films were
coated on a square Pt electrode (0.50 cm²) by dipping the
electrode into the corresponding solvents and then drying in
air. A Pt wire was used as the counter electrode, and an Ag/
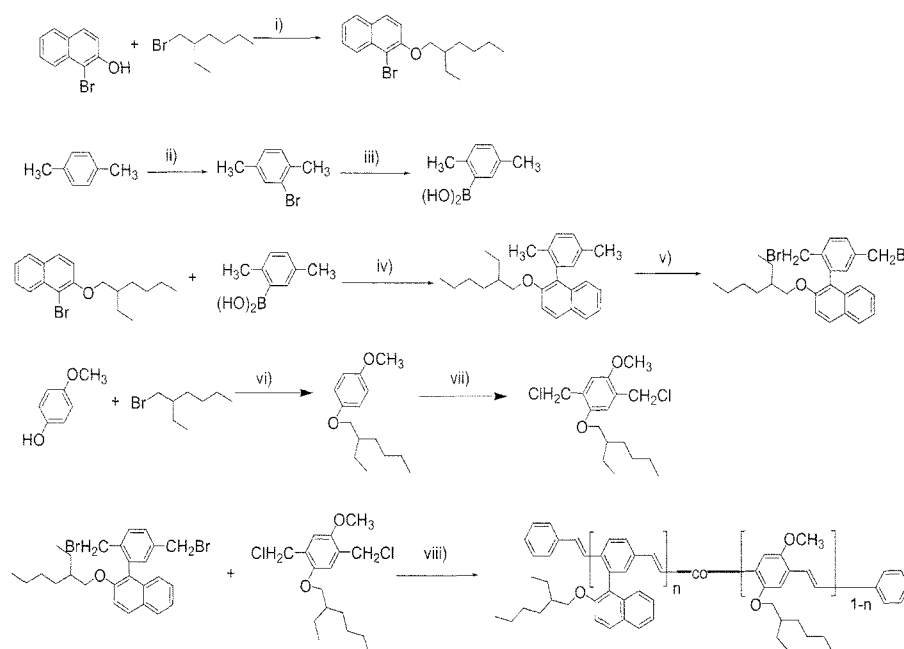
Scheme II. i) KOH, NaI, Ethanol; ii) Br₂, dichloromethane; iii) 2.5 M *n*-BuLi, trimethyl borate, ether; iv) Pd(PPh₃)₄, 2 M K₂CO₃, THF;
v) NBS, BPO, benzene; vi) KOH, NaI, ethanol; vii) 37% formaline, 37% HCl, dioxane; viii) Potassium *tert*-butoxide, 1,4-dioxane, chloromethyl benzene.

AgNO₃ (0.1M) electrode was used as the reference electrode. Prior to each series of measurements, the cell was deoxygenated with nitrogen.

Fabrication of the LED. Poly(3,4-ethylene dioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on an indium tin oxide coated glass substrate that had been washed with water, acetone, and isopropyl alcohol sequentially. A thin polymer film (1,000 Å) was spin-coated (3,000 rpm, 50 s) from a filtered (0.2 mm filter) 1.0 wt% copolymer solution in chlorobenzene on a PEDOT layer. A thin layer of LiF (5 Å) and subsequently 1,500 Å layer of Al were evaporated subsequently on the top of the emissive layer under a high vacuum (below 1×10⁻⁵ Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

Results and Discussion

The synthetic routes of the monomers and polymers are outlined in Scheme II. The EHNBMP was prepared by bromination of 1-(2,5-dimethylphenyl)-2-(2-ethylhexyloxy)-naphthalene using NBS. 1-(2,5-Dimethyl-phenyl)-2-(2-ethyl-hexyloxy)naphthalene was synthesized in a Suzuki coupling reaction of 1-bromo-2-(2-ethyl-hexyloxy)-naphthalene and 1,4-dimethylphenylboronic acid. The copolymers were obtained in a typical Gilch method. The obtained compounds and copolymers were each characterized by spectroscopic methods such as ¹H NMR and FTIR (Figure 1).

The obtained copolymers were soluble in normal organic solvents such as dichloromethane, chloroform, toluene, and *o*-dichlorobenzene. The good solubility may be due to the large alkoxy side chain and bulky naphthalene group in the EHN-PPV unit.
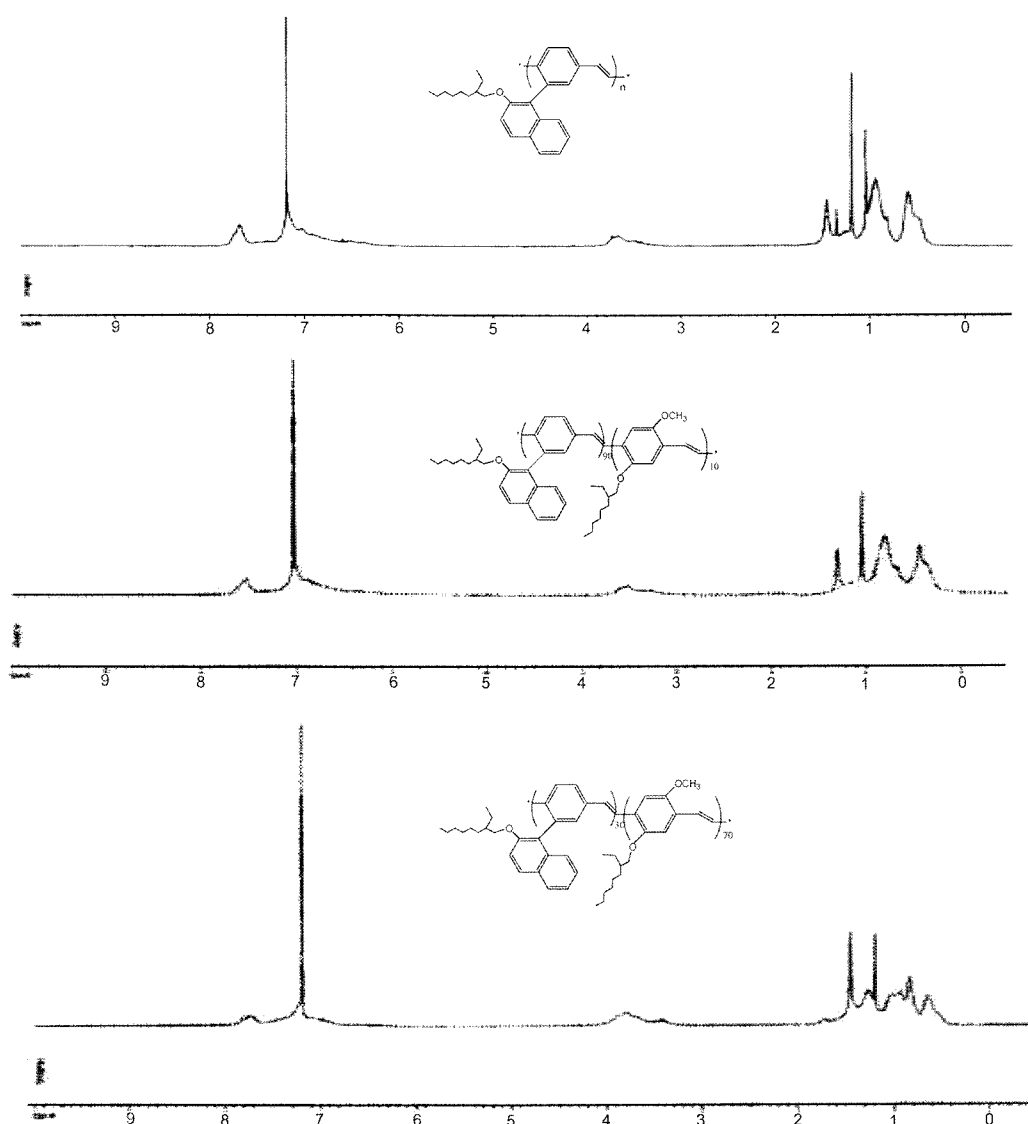

Figure 1. ¹H NMR of copolymers.

Table I. Molecular Weights of Copolymer I~VIII

Copolymers	$M_n{}^a$ ($*10^3$ g/mol)	$M_w{}^a$ ($*10^3$ g/mol)	PDI
Copolymer I	159.2	284.9	1.7
Copolymer II	227.2	346.2	1.5
Copolymer III	279.5	393.3	1.4
Copolymer IV	168.8	272.9	1.6
Copolymer V	132.6	246.6	1.8
Copolymer VI	284.9	403.4	1.4
Copolymer VII	372.6	475.1	1.3
Copolymer VIII	196.8	414.7	2.1

^{a}Copolymers were determined by gel permeation chromatography using polystyrene standards.

Table II. Optical Properties of Copolymer I~VIII

Copolymers	Solution		Film	
	UV λ_{max} (nm)^a	PL λ_{max} (nm)^a	UV λ_{max} (nm)^a	PL λ_{max} (nm)^a
Copolymer I	423	487	405	510
Copolymer II	431	488	424	511
Copolymer III	431	490	428	522
Copolymer IV	428	490	428	529
Copolymer V	434	511	429	534
Copolymer VI	452	553	444	552
Copolymer VII	468	561	452	560
Copolymer VIII	485	567	476	566

^{a}These values listed were measured in chloroform solution and thin film state onto the quartz plate.

Table I shows the molecular weights of copolymers observed by means of gel permeation chromatography (GPC). The weight-average molecular weights (M_w) were determined to range from approximately 246,000 to 475,000, and the PDI values ranged from 1.3 to 2.1. The obtained copolymers showed a relatively high molecular weight. This may have resulted from the high solubility of the copolymers during the polymerization process.

Figure 2 shows the UV-vis absorption spectra of the synthesized copolymers. The absorption spectra of the copolymer solutions were observed at the state of conc. 1 wt% in chloroform, and those of the polymer films were observed with spin-casted film on glass at the state of conc. 1 wt% in chloroform. Table II shows summarized data of the optical properties of Copolymers I~VIII. When the ratio of the EHN-PPV units increases, the PL spectrum was blue-shifted. Figure 3 shows the emission spectra of Copolymers I~VIII in the solution state. It is suggested that the presence of increased EHN-PPV units leads to a non-coplanar backbone
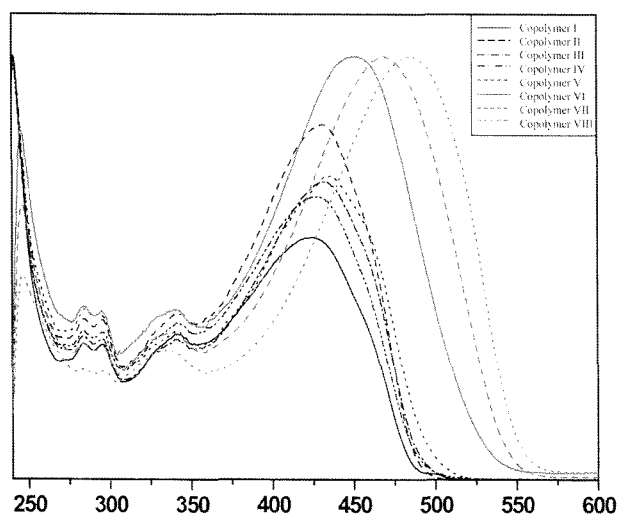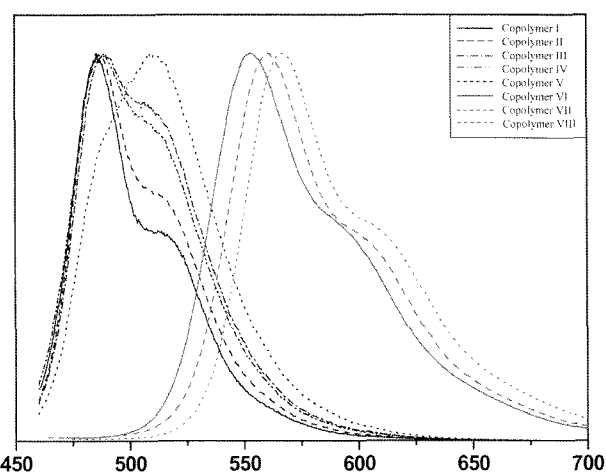

Figure 3. PL spectra of copolymer I~VIII in CHCl$_3$.

**Figure 2.** UV-Visible spectra of copolymer I~VIII in CHCl$_3$ solutions.

condition due to the steric effects of bulky side chains, and shortens the conjugation length. It was also observed that an increment of MEH-PPV units including many electron-donating moieties leads to an extended conjugation length and red shifting. Hence, suitable control of the ratio of EHN-PPV units to MEH-PPV units causes the color to become tunable from the green to the orange light region.

The thermal stabilities of the copolymers were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C/min. Weight losses of 5% in the copolymers were observed at temperatures greater than 380 °C. The glass-transition temperatures (T_g) of the copolymers were determined to range from 84 to 119 °C. The copolymers showed an increase in the T_g values as the number of EHN-PPV units increased.

Cyclic voltammetry (CV) was employed to estimate the HOMO and LUMO energy levels. The electrochemical process probed by cyclic voltammetry is similar to that involved

Table III. Electrochemical Data of Copolymer I~VIII

Copolymers	HOMO (eV)	LUMO (eV)	UVedge (nm)	Optical Band Gap
Copolymer I	5.71	3.14	483	2.57
Copolymer II	5.72	3.15	483	2.57
Copolymer III	5.72	3.16	485	2.56
Copolymer IV	5.72	3.16	485	2.56
Copolymer V	5.77	3.24	490	2.53
Copolymer VI	5.36	3.06	538	2.30
Copolymer VII	5.30	3.04	548	2.26
Copolymer VIII	5.31	3.08	555	2.23
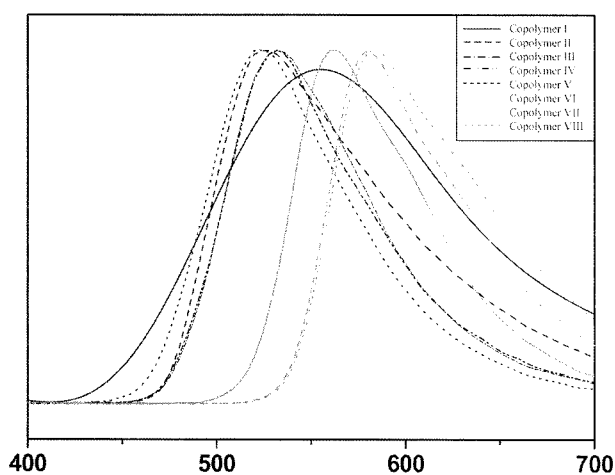
Figure 4. EL spectra of ITO/PEDOT/copolymer I~VIII/ LiF/Al.

in the charge injection and transport process in LED devices. The polymer film was coated onto a Pt electrode and scanned positively and negatively at a scan rate of 100 mVs^{-1} in a 0.1 M solution of Bu$_4$NClO$_4$ in anhydrous acetonitrile. The experiments were calibrated with a standard ferrocene/ferrocenium (Fc) redox system with an assumed energy level of Fc at 4.8 eV in a vacuum.[38,39] Table III summarizes the electrochemical data of Copolymers I~VIII. It was observed that a higher ratio of MEH-PPV units lead to a higher highest occupied molecular orbital (HOMO) level. This can be explained by the electron donating effect of the alkoxy group of the MEH-PPV units.

Figure 4 shows the λ_{max} of EL spectra of the fabricated device, which includes synthesized Copolymers I~VIII as an emitting layer. The device structure was ITO/ PEDOT/ copolymers/LiF/Al, with the conducting polymer poly(3,4-ethylene dioxythiophene) (PEDOT) as the hole injection layer, LiF as the electron injection layer, ITO as the anode and Al as the cathode. Table IV also shows the maximum peaks of each copolymer. A blue shift was observed with the increment of the ratio of EHN-PPV units, as expected in the PL spectra. It is possible that adequate control the ratio
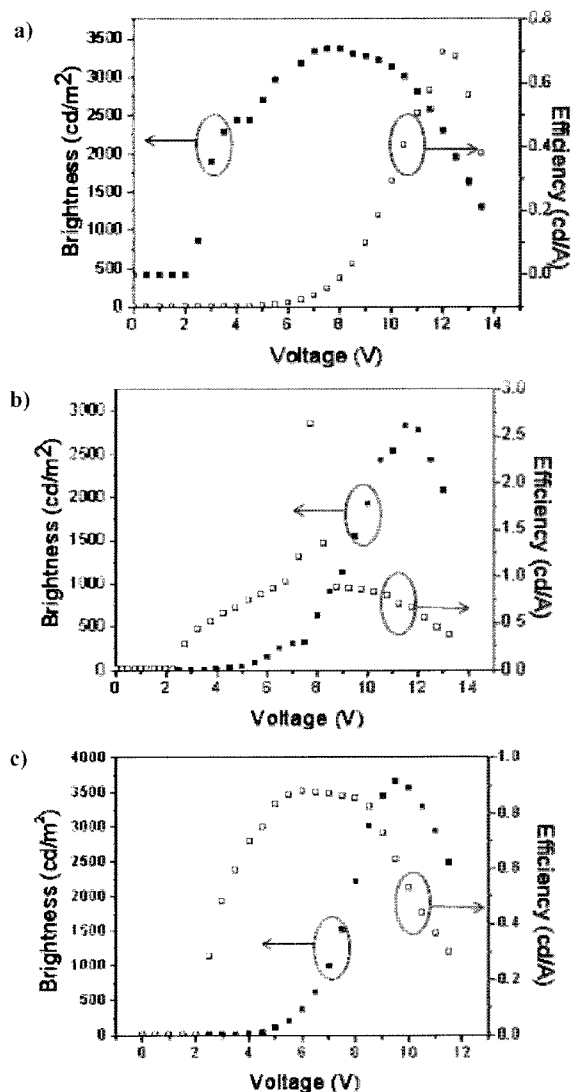
Figure 5. Characteristics of brightness *versus* applied voltage and efficiency *versus* applied voltage of copolymer VI(a), VII(b), and VIII(c).

Table IV. EL Maximum of ITO/PEDOT/Copolymer I~VIII/KiF/Al

Copolymers	EL λ_{max} (nm)
Copolymer I	532
Copolymer II	528
Copolymer III	532
Copolymer IV	532
Copolymer V	540
Copolymer VI	564
Copolymer VII	580
Copolymer VIII	584

of EHN-PPV to MEH-PPV leads to color tunability from the green to the orange light emission range.

Table V. Device Performances of the ITO/PEDOT/Copolymer I~VIII/LiF/Al Devices in Air at Room Temperature

| Copolymers	Turn-on Voltage (V)	Max. Luminance Efficiency (cd/A)	Max. Power Efficiency (lm/W)	Max. Brightness (cd/m^2)
Copolymer I	6	0.001	0.0004	3.6 (13 V)
Copolymer II	4.5	0.076	0.0300	367.1 (12 V)
Copolymer III	4.5	0.163	0.0604	619.1 (12.5 V)
Copolymer IV	3	0.052	0.0325	376.2 (8 V)
Copolymer V	3	0.006	0.0039	75 (6 V)
Copolymer VI	2.5	0.708	0.4012	3321 (12 V)
Copolymer VII	2.5	2.625	1.0641	2828 (11.5 V)
Copolymer VIII	2.5	0.878	0.5468	3657 (9.5 V)
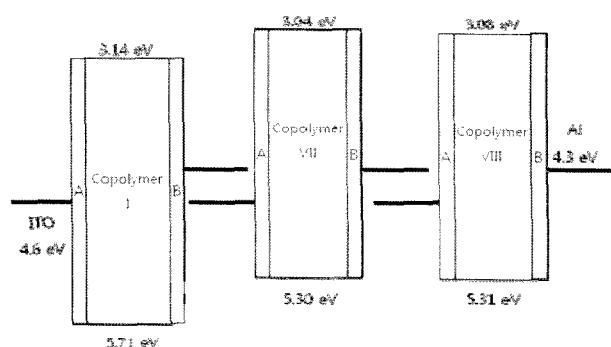
Figure 6. Energy level diagrams for the materials used in the OLED fabrication (A: PEDOT, B: LiF).

Figure 5 shows the characteristics of the brightness and efficiency *versus* the applied voltage of Copolymers VI~VIII, and Table V shows the EL device performances of Copolymers I~VIII. The turn-on voltage was 6~2.5 V; as the ratio of the EHN-PPV units increases, the turn-on voltage also increased. The maximum efficiency of the copolymer was increased by the ratio of MEH-PPV units up to a ratio of 50:50. Copolymer VII with a 50:50 composition showed the maximum luminance efficiency of 2.5 cd/A and a maximum brightness of 2,828 cd/m^2. These results can be explained by the better charge balance between the holes and the electrons. Figure 6 shows device band diagrams of the devices. Device VII with Copolymer VII as an emitting material shows a low hole injection barrier compared to the other devices. From the results shown in the band diagram, it is suggested that a low hole injection barrier leads to higher device efficiency. This is feasible in that an electron can be easily injected by LiF as an electron injection layer. Thus, easier hole injection can lead to a better charge balance.

Conclusions

Copolymers derived from MEH-PPV and naphthyl-substituted EHN-PPV were synthesized as an efficient emitter.

The obtained copolymers showed good solubility and a high molecular weight. As the ratio of EHN-PPV units increased, the PL spectrum was blue-shifted. As the content of MEH-PPV to EHN-PPV was increased to a ratio of 50:50, the maximum brightness, quantum efficiency, and power efficiency of the device increased gradually and the turn-on voltage decreased. These results can be explained by the better charge balance between the holes and the electrons.

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