

Synthesis and Characterization of Novel Light-Emitting Copolymers with Electron-Withdrawing Substituents

Sung-Ho Jin*, Dae-Sung Koo, Chan-Koo Hwang, Jung Yun Do, and Young-Inn Kim

Department of Chemistry Education and Center for Plastic Information System,
Pusan National University, Busan 609-735, Korea

Yeong-Soon Gal

Polymer Chemistry Lab., Kyungil University, Hayang 712-701, Korea

Jae Wook Lee

Department of Chemistry, Dong-A University, Busan 604-714, Korea

Jin-Taek Hwang

Department of Materials Sci. & Eng., Gwangju Institute of Science and Technology, Gwangju 500-712, Korea

Received October 17, 2004; Revised February 14, 2005

Abstract: We synthesized two new series of alternating copolymers, poly[bis(2-(4-phenylenevinylene)-2-cyanoethenyl)-9,9-dihexyl-9H-fluoren-2,7-yl-*alt*-1,4-phenylene] (Polymer-I) and poly[bis(2-(4-phenylenevinylene)-2-cyanoethenyl)-9,9-dihexyl-9H-fluoren-2,7-yl-*alt*-2,7-(9,9-dihexylfluorene)] (Polymer-II), via the Suzuki coupling reaction, for use in light-emitting diodes (LEDs). Defect-free uniformly thin films of these polymers were found to be easily formed on indium-tin oxide (ITO) coated glass substrates. Multi-layer LEDs with ITO/PEDOT/Polymer/LiF/Al configurations with or without an Alq₃ electron transport layer were fabricated with these polymers. The maximum EL emissions of Polymer-I and Polymer-II with an Alq₃/LiF/Al cathode were observed at 516 and 533 nm, respectively. The maximum brightness and external luminance efficiency of the devices fabricated with the EL polymers were found to be 411 cd/m² and 0.16 cd/A, respectively.

Keywords: electroluminescence, light-emitting polymer, light-emitting diode, luminescence efficiency.

Introduction

The emission of light from organic and polymeric materials in response to an applied field in organic light-emitting diodes (OLEDs) is currently generating a great deal of interest as a possible alternative to liquid crystal displays (LCDs) for certain applications. OLEDs offer the possibility of efficient low-voltage full-color displays. Since Tang and Vanslyke fabricated high-efficiency OLEDs consisting of light-emitting layers and carrier transport layers,^{1,2} various kinds of electroluminescent (EL) polymers as well as organic fluorescent dyes have been developed to obtain materials with high efficiency, long lifetimes and even white-color emission, which can be used as LCD back-lights.³

Since the first report by the Cambridge group of polymer LEDs (PLEDs) based on poly(*p*-phenylenevinylene) (PPV),⁴ a great variety of polymers with different color emissions,⁵⁻⁷ electron affinities,^{8,9} ionization potentials,^{10,11} and photoluminescence (PL) efficiencies have been synthesized, and their EL properties have been extensively studied. Among the various types of EL polymers, PPVs,^{12,13} poly(9,9-dialkylfluorene)s (PFs)^{14,15} and their derivatives are considered to be promising candidate materials for use in PLEDs.

The advantage of EL polymers is the feasibility of the design of their molecular structure to improve their solubility and adjust their HOMO and LUMO energy levels. The copolymerization method has been widely used in the preparation of EL polymers to achieve easy tuning of emission color through control of their intermolecular and intramolecular energy transfer and their physical properties. A number of PF derivatives are suitable wide-band gap materials because of facile substitution at the carbon 9 position of the

*e-mail: shjin@pusan.ac.kr

1598-5032/04/114-06©2005 Polymer Society of Korea

fluorene unit, which can be used to improve their processability and their PL and EL efficiencies. A variety of fluorene-based alternating and random copolymers have been synthesized using fluorenes and other aromatic compounds, which fully cover the red, green, and blue emission color regions of the visible spectrum.^{16,17}

Greenham *et al.* first reported that an electron-transporting polymer, poly(*p*-phenylenecyanovinylene) (CN-PPV), exhibits a very high internal efficiency (4%) in PLEDs.⁷ A variety of CN-PPV derivatives have since been synthesized.¹⁸ These polymers have high electron affinities because of the strong electron-withdrawing cyano groups on their polymer backbones. The energy barrier between the cathode and the emissive layer can then be reduced with a high work function aluminum cathode, and in turn the stability of such devices can be improved. In our research into improving the performance of PLEDs, we have synthesized and characterized novel EL polymers such as alkylsilylphenyl-, alkyloxyphenoxy-, and 1,3,4-oxadiazole-substituted PPVs, blending systems with oxadiazole containing electron transfer polymers, and alternating copolymers composed of PPV segments and aromatic amine blocks.¹⁹⁻²⁶

In this paper, we report the synthesis of novel EL copolymers with electron-withdrawing cyano substituents on the vinylene units in bis(cyanophenylenevinylene)fluorenyl moieties and phenylene or fluorene repeating units along the polymer backbone, and characterized their electro-optical properties.

Experimental

Synthesis of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2). To a solution of 1,4-dibromobenzene (5 g, 21 mmol) in THF (70 mL) at -78 °C, *n*-butyllithium (17.64 mL, 2.5 M in hexane) was added by syringe. The mixture was stirred at -78 °C, warmed to 0 °C for 15 min, and cooled again to -78 °C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.46 g, 51 mmol) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with diethyl ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporator, and the residue was purified by column chromatography (eluent: *n*-hexane:ethyl acetate=10:1) to provide 3.0 g (43%) of product as a white solid.

¹H NMR (CDCl₃, ppm): 7.65 (d, 2H, ArH), 7.50 (d, 2H, ArH), 1.35 (s, 24H, CH₃). ¹³C NMR (CDCl₃, ppm): 136.1, 130.8, 84.1, 25.0.

Synthesis of 9,9-dihexylfluorenyl-2,7-diboronic Acid. A mixture of 2,7-dibromo-9,9-dihexylfluorene (12.1 g, 24.6 mmol) in 200 mL of dry THF was added dropwise to magnesium turnings (3 g, 0.12 mol). When the addition was complete, the solution was refluxed for 1 h. This solution

was added in drops over a period of 2 h into a solution of trimethyl borate (30.7 mL, 0.27 mol) in 200 mL of dry THF at -78 °C. The temperature was gradually raised overnight to room temperature. The mixture was added to a stirred mixture of crushed ice (500 g) and concentrated sulfuric acid (30 mL). The aqueous layer was extracted with diethyl ether. The combined organic layer was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash column chromatography (eluent: *n*-hexane:ethyl acetate=10:1) and by recrystallization from ethyl acetate to give a white solid (5.0 g, 48%).

¹H NMR (CDCl₃, ppm): 7.85 (d, 2H, ArH), 7.65 (d, 4H, ArH) 1.92 (m, 4H; α -CH₂ of hexyl group at 9-position of fluorene), 1.06 (12H; β - δ -CH₂), 0.76-0.75 (10H, ϵ -CH₂ and CH₃).

Synthesis of 9,9-dihexylfluorenyl-2,7-bis(trimethylene boronate) (3). 9,9-Dihexylfluorenyl-2,7-diboronic acid (3.0 g, 7.1 mmol), trimethylene glycol (1.03 mL, 14.9 mmol) and toluene (100 mL) were placed in a three-neck flask and the mixture was refluxed under nitrogen for 24 h. The solvent was evaporated to dryness and the residue was purified by flash column chromatography (eluent: *n*-hexane:ethyl acetate=10:2) and by recrystallization from hexane to give a white solid (1.6 g, 45 %).

¹H NMR (CDCl₃, ppm): 7.75 (d, 6H, ArH), 4.21 (s, 8H, -CH₂-), 2.1 (s, 4H, -CH₂-), 1.96 (m, 4H; α -CH₂ of hexyl group at 9-position of fluorene), 1.06 (12H; β - δ -CH₂), 0.76-0.75 (10H, ϵ -CH₂ and CH₃). ¹³C NMR (CDCl₃, ppm): 14.0, 22.6, 23.7, 27.4, 30.0, 31.5, 40.3, 54.9, 62.0, 119.1, 127.8, 132.3, 143.5, 150.3. Anal. Calcd for C₃₁H₄₄B₂O₄: C 74.13, H 8.83. Found: C 74.29, H 8.48.

Synthesis of Poly[bis(2-(4-phenylenevinylene)-2-cyanoethenyl)-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-1,4-phenylene] (Polymer-I). This polymer was prepared by using the Suzuki coupling reaction between 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (1) and 1,4-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2). A mixture of 1.0 g (1.34 mmol) of compound 1, 0.44 g (1.34 mmol) of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene, and 9 mg (0.0078 mmol) of Pd(PPh₃)₄ in 15 mL toluene was stirred at 90 °C. To this flask, 5 mL of aqueous 2 M Na₂CO₃ was added, and the mixture was stirred for 2 days at 100 °C. The hot reaction mixture was poured into 500 mL of methanol to precipitate the polymer. The collected polymer was redissolved in 100 mL of chloroform and then washed with 400 mL of deionized water. The water layer was decanted carefully. The catalyst particles in the polymer solution were removed by filtration, followed by evaporation of the solvent using a rotary evaporator. The polymer was dissolved in a small amount of chloroform and then poured into methanol. The polymer was collected by filtration and dried under vacuum (0.53 g, 47%).

¹H NMR (CDCl₃, ppm): 8.0-7.4 (br, 20H, vinylic proton and ArH), 2.1-1.8 (br, 4H; α -CH₂ of hexyl group at 9-posi-

tion of fluorene), 1.2-0.9 (br, 12H; β - δ -CH₂-), 0.8-0.6 (10H, ϵ -CH₂- and CH₃). Anal. Calcd for C₄₉H₄₆N₂: C 88.77, H 7.00, N 4.23; Found: C 83.75, H 7.33, N, 4.34.

Poly[bis(2-(4-phenylenevinylene)-2-cyanoethenyl)-9,9-dihexyl-9H-fluoren-2,7-yl-*alt*-2,7-(9,9-dihexylfluorene)]

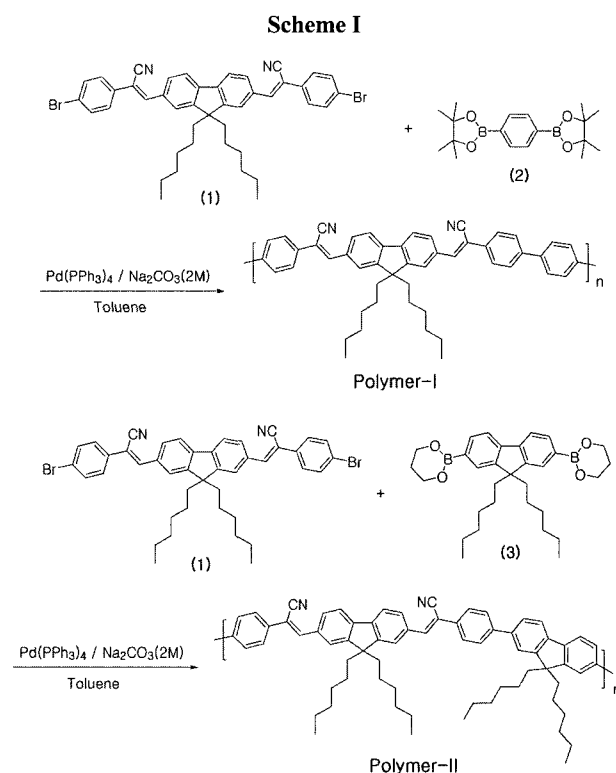
(**Polymer-II**) was synthesized with the same procedure used for Polymer-I (0.37 g, 30 %).

¹H NMR (CDCl₃, ppm): 8.0-7.3 (br, 22H, vinylic proton and ArH), 2.1-1.8 (br, 8H; α -CH₂ of hexyl group at 9-position of fluorene), 1.2-0.9 (br, 24H; β - δ -CH₂-), 0.8-0.6 (20H, ϵ -CH₂- and CH₃). Anal. Calcd for C₆₆H₇₄N₂: C 88.53, H 8.34, N 3.13; Found: C 83.42, H 8.64, N, 3.20.

Measurements. ¹H and ¹³C NMR spectra were recorded using a Bruker AM-300 spectrometer; chemical shifts were recorded in ppm. The UV-visible spectra were recorded on a Shimadzu UV-3100 spectrophotometer with baseline corrections and normalizations carried out using Microsoft Origin software. The molecular weights and polydispersities of polymers were determined with gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, Plgel 5 μ m MIXED-C, refractive index detector) in THF solution. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851^o under a nitrogen atmosphere at a heating rate of 10^oC/min. Emission spectra of dilute (~10⁻⁶ M) solutions of the polymers were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Solid-state emission measurements were carried out using films supported on glass substrates and mounted with front-face excitation at an angle of < 45^o. Each polymer film was excited with several portions of visible light from a xenon lamp. To measure the EL of the polymers, the PLEDs were constructed as follows. A glass substrate coated with a transparent ITO electrode was thoroughly cleaned with successive ultrasonic treatments in acetone, isopropyl alcohol, and distilled water, and dried by heating under nitrogen gas. The polymer film was then prepared by spin casting a polymer chlorobenzene or 1,2-dichlorobenzene solution (0.5-1.5 wt%). Uniform and pinhole-free films with a thickness around 100 nm were easily obtained from the resulting polymer solutions. Alq₃, LiF, and aluminum metal were deposited on top of the polymer films through a mask by vacuum evaporation at pressures below 1 \times 10⁻⁶ torr, yielding active areas of 4 mm². To determine the device characteristics, the current density-voltage-luminescence (*J-V-L*) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (CS-1000, LS-100). All procedures and measurements described above were carried out in the open air at room temperature.

Results and Discussion

The monomers 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (1), 1,4-bis(4,4,5,5-tetramethyl-



1,3,2-dioxaborolan-2-yl)benzene (2), and 9,9-dihexylfluorenyl-2,7-bis(trimethylene boronate) (3) were synthesized according to procedures from the literature with slight modifications.^{26,27} The statistical alternating EL copolymers were synthesized from 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (1) and aromatic diboronic derivatives (2 or 3) as comonomers with Suzuki coupling reactions as shown in Scheme I. The Suzuki polymerizations were carried out with Pd(PPh₃)₄ and aq. Na₂CO₃ in toluene. The resulting EL polymers were purified by successive Soxhlet extraction with different solvents including methanol and hexane, and finally dissolved in CHCl₃ and reprecipitated into methanol.

The molecular structures and purities of the monomers and the corresponding EL polymers were determined with ¹H and ¹³C NMR spectroscopy, and with elemental analysis. The weight average molecular weights (*M_w*) and polydispersities of Polymer-I and Polymer-II were found to be 10.1 \times 10³ and 1.7, and 69.6 \times 10³ and 3.3, respectively. The thermal stability of each polymer was investigated with TGA under a nitrogen atmosphere. Polymer-I and Polymer-II exhibit a high thermal stability, with their 5% weight losses occurring at 358 and 290 ^oC respectively.

Figure 1 shows the ¹H NMR spectra of 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (a), 9,9-dihexylfluorenyl-2,7-bis(trimethylene boronate) (b) and Polymer-II (c) in CDCl₃. Because the polymerization method used coupling reactions between two monomers, the ¹H NMR spectrum of Polymer-II was found to be almost identical to

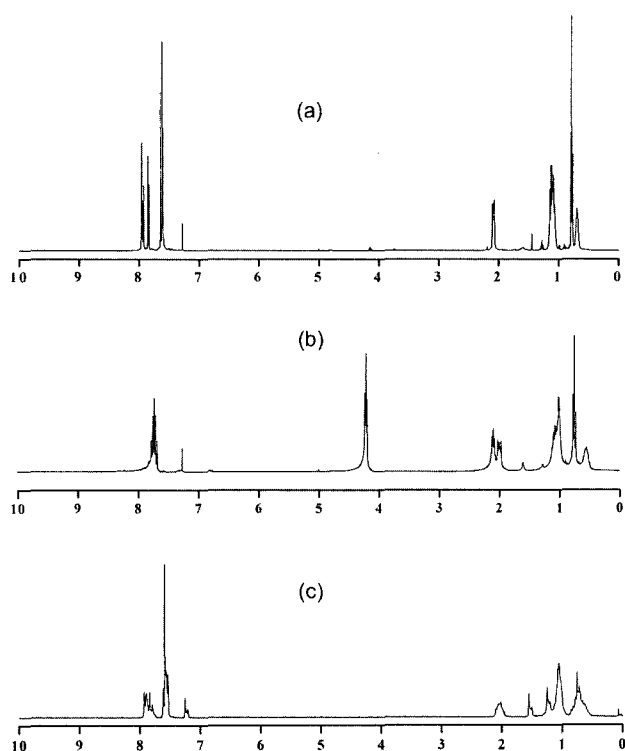


Figure 1. ^1H NMR spectra of 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (a), 9,9-dihexylfluorenyl-2,7-bis(trimethylene boronate) (b), and Polymer-II (c) in CDCl_3 .

those of the corresponding monomers. High quality optical thin films of the polymers without any defects could be spun cast onto the ITO-coated glass substrates.

Figure 2 displays the optical absorption and emission spectra of thin films of the polymers. The maximum absorption peaks of Polymer-I and Polymer-II are at 400 and 419 nm with onset absorption peaks at 462 and 484 nm respectively. From the onsets of the absorption spectra, the band gaps of Polymer-I and Polymer-II were found to be 2.68 and 2.56 eV respectively. The PL spectra of thin films of the polymers were recorded with excitation wavelengths corresponding to the wavelength of their absorption maxima. The maximum emission peaks of Polymer-I and Polymer-II were

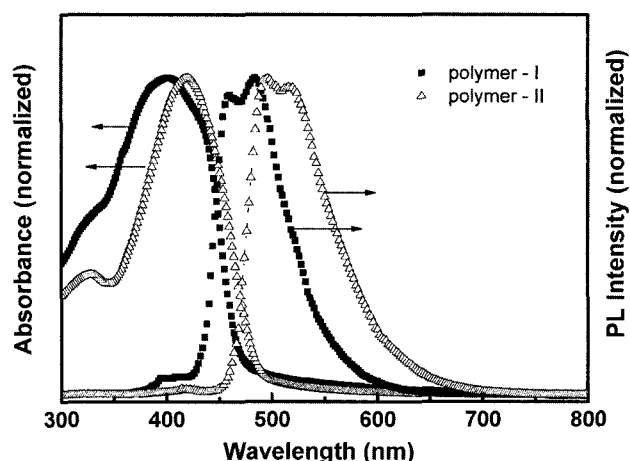


Figure 2. UV-visible absorption and PL spectra of polymers in film state.

found to be 483 and 496 nm with shoulder peaks at 460 and 518 nm respectively, which correspond to a greenish blue color. Because of the rigid biphenyl structure of the polymer backbone of Polymer-I, the maximum emission peak of Polymer-I is blue-shifted by about 13 nm with respect to that of Polymer-II.

The energy band diagrams for Polymer-I and Polymer-II were obtained by using cyclic voltammetry to determine the HOMO binding energies with respect to ferrocene standard which were found to be almost the same, 6.05 eV. The LUMO levels were calculated approximately by subtracting the optical band gaps from the HOMO binding energies. The replacement of the protons of the vinylene units with electron-withdrawing cyano groups was found to lower the LUMO levels of Polymer-I and Polymer-II (3.37 and 3.35 eV respectively) with respect to those of MEH-PPV (3.0 eV) and PPV (2.6 eV). Thus these new EL polymers are expected to have improved electron injection ability. Furthermore, the introduction of a 1 nm thick LiF electron injection layer means that electrons can be more easily injected into Polymer-I and Polymer-II than holes. The electro-optical properties of Polymer-I and Polymer-II are summarized in Table I.

We fabricated multi-layer PLEDs with the ITO/PEDOT/

Table I. Electro-Optical Data and EL Characteristics of ITO/PEDOT/Polymer/LiF/Al and ITO/PEDOT/Polymer/Alq₃/LiF/Al Device

Sample	Cathode	λ_{max} (nm) ^a			Turn-on Voltage (V)	L_{max} (cd/m ²) ^b	η_{max} (cd/A) ^c
		UV	PL	EL			
Polymer-I	LiF/Al	400	483, 460 ^d	520	5.0	41	0.03
	Alq ₃ /LiF/Al	-		516	5.0	138	0.15
Polymer-II	LiF/Al	419	496, 518 ^d	515	5.0	32	0.02
	Alq ₃ /LiF/Al	-		533	7.0	411	0.16

^aMeasured in film state onto the fused silica substrate. ^bMaximum luminescence. ^cMaximum luminance efficiency. ^dShoulder.

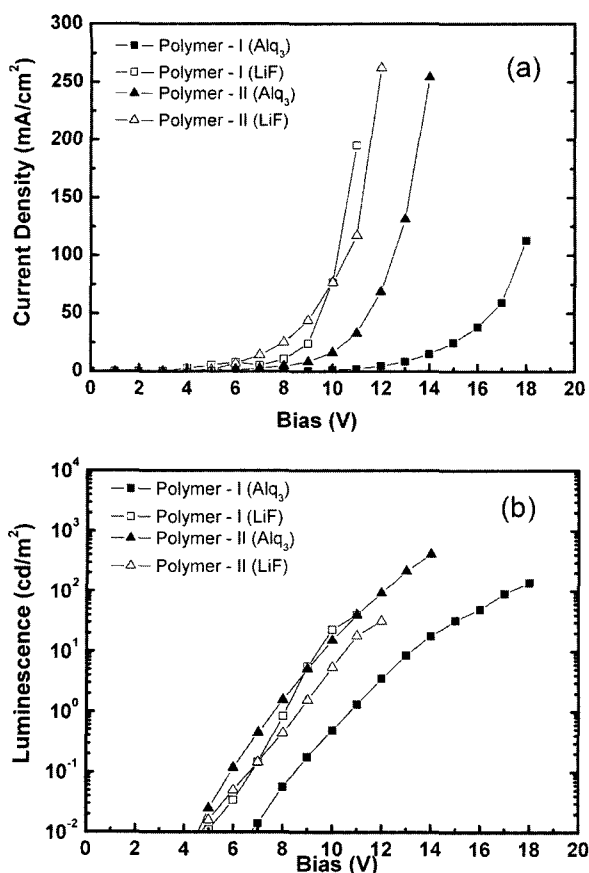


Figure 3. Current density-voltage (a) and voltage-luminescence (b) characteristics of ITO/PEDOT/Polymer/LiF/Al and ITO/PEDOT/Polymer/Alq₃/LiF/Al devices.

Polymer/cathode configurations using two types of cathode structures. The cathodes were fabricated with a LiF (1 nm)/Al (200 nm) bilayer (device 1) or a triple layer of Alq₃ (20 nm)/LiF (1 nm)/Al (200 nm) (device 2).

Figure 3 shows the current density-voltage (J - V) and luminescence-voltage (L - V) characteristics of devices 1 and 2. The current densities and luminescence intensities of the two devices increase exponentially with increasing forward bias voltage above the turn-on voltage, and the EL devices exhibit excellent diode characteristics. Turn-on voltages of the resulting EL polymers are about 5.0 V for current and luminescence. The maximum brightnesses of the Polymer-I and Polymer-II devices were found to be 138 cd/m² at 18 V and 411 cd/m² at 14 V, respectively.

Figure 4 shows the EL spectra of Polymer-I and Polymer-II for the different device configurations. The EL spectra of Polymer-I and Polymer-II are almost identical to their PL spectra, which indicate that their emission mechanisms are the same as for their excitation processes and that the Alq₃ layer serves as an electron transport layer.

Figure 5 displays the plots luminous efficiency versus current density for devices 1 and 2. The maximum luminous

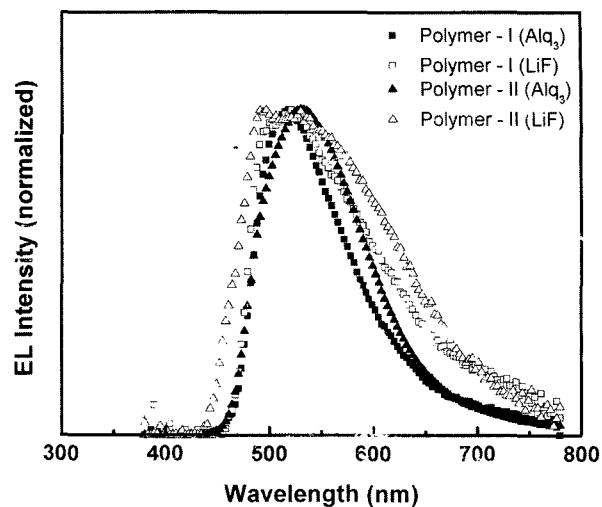


Figure 4. EL spectra of ITO/PEDOT/Polymer/LiF/Al and ITO/PEDOT/Polymer/Alq₃/LiF/Al devices.

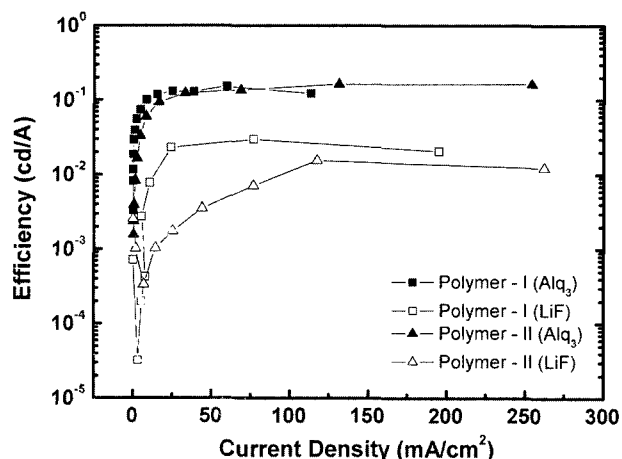


Figure 5. Current density-luminous efficiency curves of ITO/PEDOT/Polymer/LiF/Al and ITO/PEDOT/Polymer/Alq₃/LiF/Al device.

efficiencies of Polymer-I and Polymer-II with a triple layer Alq₃/LiF/Al cathode were found to be 0.15 and 0.16 cd/A respectively, which are 7 times higher than those of the devices with LiF/Al bilayer cathodes. The EL characteristics and performances of the devices using EL Polymer-I and Polymer-II are also summarized in Table I. Further optimization of these EL devices by using a low work function metal, such as calcium cathode, as the cathode is expected to result in better EL performance.

Conclusions

We have tested the introduction of electron-withdrawing cyano groups into the vinylene units of EL polymers to increase their electron affinity and improve their electron

injection properties. The resulting statistical alternating copolymers were synthesized via Suzuki coupling reactions. These EL polymers were found to exhibit good solubility in common organic solvents. The UV-visible absorption spectra of the copolymers contain strong absorption bands at 400 and 419 nm, which correspond to the π - π^* transitions of their main chain structures. The turn-on voltages of devices containing these EL polymers in the ITO/PEDOT/Polymer/cathode configuration with different cathodes were found to be 5.0 V. The emission colors of the statistical alternating copolymers were found to be greenish blue. The maximum brightnesses and luminous efficiencies of these devices were 411 cd/m² at 14 V and 0.16 cd/A at 13 V respectively.

Acknowledgements. We gratefully acknowledge the support of the Ministry of Information & Communications, Korea, under the Information Technology Research Center (ITRC) Support Program.

References

- (1) C. W. Tang and S. A. VanSlyke, *Appl. Lett.*, **51**, 913 (1987).
- (2) S. A. VanSlyke, P. S. Bryan, and C. W. Tang, *Proceedings of the 8th International Workshop on Inorganic and Organic Electroluminescence*, Berlin, Germany, 1996, pp 195.
- (3) J. Kido, H. Shionoya, and K. Nagai, *Appl. Phys. Lett.*, **67**, 2281 (1995).
- (4) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **347**, 539 (1990).
- (5) G. Grem, G. Leditzky, B. Ullrich, and G. Leising, *Adv. Mater.*, **4**, 36 (1992).
- (6) D. H. Hwang, H. K. Shim, J. I. Lee, and K. S. Lee, *J. Chem. Soc., Chem. Commun.*, 2461 (1994).
- (7) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, *Nature*, **365**, 628 (1993).
- (8) Y. Q. Liu, X. Z. Jiang, Q. L. Li, and D. B. Zhu, *Synth. Met.*, **4**, 36 (1997).
- (9) Z. Peng, Z. Bao, and M. E. Galving, *Adv. Mater.*, **10**, 680 (1998).
- (10) Y. Q. Liu, M. S. Liu, X. C. Li, and A. K. Y. Jen, *Chem. Mater.*, **10**, 3301 (1998).
- (11) X. C. Li, Y. Q. Liu, M. S. Liu, and A. K. Y. Jen, *Chem. Mater.*, **11**, 1568 (1999).
- (12) M. D. Johansson, X. Wang, T. Johansson, O. Inganäs, G. Yu, G. Srdanov, and M. R. Andersson, *Macromolecules*, **35**, 4997 (2002).
- (13) H. Spreitzer, H. Becker, E. Kluge, W. Kreuder, H. Schenk, R. Demandt, and H. Schoo, *Adv. Mater.*, **10**, 1340 (1998).
- (14) M. T. Bernius, M. Inbasekaran, J. O'Brien, and W. S. Wu, *Adv. Mater.*, **12**, 1737 (2000).
- (15) J. Ding, M. Day, G. Robertson, and J. Roovers, *Macromolecules*, **35**, 3474 (2002).
- (16) U. Scherf and E. J. List, *Adv. Mater.*, **14**, 477 (2002).
- (17) A. D. Bouillud, I. Lévesque, Y. Tao, M. DiIorio, S. Beaupré, P. Blondin, M. Ranger, J. Bouchard, and M. Leclerc, *Chem. Mater.*, **12**, 1931 (2000).
- (18) X. Zhan, S. Wang, Y. Liu, X. Wu, and D. Zhu, *Chem. Mater.*, **15**, 1963 (2003).
- (19) S. H. Jin, J. E. Jung, D. K. Park, B. C. Jeon, S. K. Kwon, Y. H. Kim, D. K. Moon, and Y. S. Gal, *Eur. Polym. J.*, **37**, 921 (2001).
- (20) J. H. Lee, H. S. Yu, W. Kim, Y. S. Gal, J. H. Park, and S. H. Jin, *J. Polym. Sci.; Part A: Polym. Chem.*, **38**, 4185 (2000).
- (21) S. H. Jin, Y. K. Sun, B. H. Sohn, and W. H. Kim, *Eur. Polym. J.*, **36**, 957 (2000).
- (22) S. H. Jin, M. S. Jang, H. S. Suh, H. N. Cho, J. H. Lee, and Y. S. Gal, *Chem. Mater.*, **14**, 643 (2002).
- (23) S. H. Jin, H. J. Park, J. Y. Kim, K. Lee, S. P. Lee, D. K. Moon, H. J. Lee, and Y. S. Gal, *Macromolecules*, **35**, 7532 (2002).
- (24) S. H. Jin, S. Y. Kang, M. Y. Kim, U. C. Yoon, J. Y. Kim, K. Lee, and Y. S. Gal, *Macromolecules*, **36**, 3841 (2003).
- (25) S. H. Jin, M. Y. Kim, J. Y. Kim, K. Lee, and Y. S. Gal, *J. Am. Chem. Soc.*, **126**, 2474 (2004).
- (26) S. H. Jin, M. Y. Kim, S. H. Park, K. Lee, and Y. S. Gal, *Chem. Mater.*, **16**, 3299 (2004).
- (27) W. L. Yu, J. Pei, Y. Cao, W. Huang, and A. J. Heeger, *Chem. Commun.*, 1837 (1999).