

New Deep Blue Light Emitting Copolymer Containing Fluorene, Carbazole, and Dialkoxynaphthalene

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Received 24 August 2009; accepted 6 February 2010

DOI 10.1002/app.33599

Published online 16 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: We synthesized the new copolymer, which was composed of dialkoxy naphthalene, *N*-alkylcarbazole, and fluorine, by Suzuki coupling reaction. The resulting copolymer was soluble in common organic solvents and showed the weight-average molecular weight (M_w) of 288,000 with a polydispersity index of 2.56. Cyclic voltammetry and UV-vis study revealed that the HOMO

energy level and optical band gap of copolymer was 5.66 and 3.03 eV, respectively. The ITO/PEDOT/polymer/LiF/Al device emits bright deep blue light with a maximum peak around 422 nm. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 43–48, 2011

Key words: fluorescence; light-emitting diodes; copolymers

INTRODUCTION

Considerable progress has been made since the initial discovery of conjugated polymer electroluminescence by Burroughes et al. in 1989.¹ In particular, polymer light emitting diodes (LEDs) can now achieve high brightness and efficiency and their operation lifetimes are improving rapidly.^{2,3} Full color display applications required red, green, and blue emission and whilst all three colors have been demonstrated, there are relatively few efficient and high brightness blue emission polymers.^{4–6} Furthermore, the blue light emitting polymers (LEPs) are very important for the development of cost-efficient white LEDs for next-generation applications such as general light and backlight source for LCD.^{7–9} Therefore, developing efficient, stable, and deep blue LEPs is essential to realize such applications.

The first reported blue LEP was poly(*p*-phenylene).¹⁰ Other blue light-emitting conjugated polymers have since been demonstrated, including polyphenylene derivatives,¹¹ poly(dialkylfluorene) derivatives,^{12,13} and poly(phenylene vinylene) derivatives.^{14–16}

Among them, poly(dialkylfluorene) derivatives have become the subject of considerable attention. They are considered by several researchers and industrial groups as the most promising blue light emitting material due to the chemical and thermal stability, high photoluminescence quantum efficiency and easy processability through an introduction of solubilizing groups in the 9-position of the fluorene ring.¹⁷ And, the physicochemical properties of them can be tuned via side chain substitution without substantial changing the electronic properties of backbone.¹⁸ Band gap and energy level engineering, however, can be readily achieved via copolymerization.^{19,20}

It was also found that the introduction of rigid and bulky naphthyl group improved thermal stability with higher glass-transition temperatures and prevented the generation of excimers due to molecular interaction.^{21–23} Therefore, it creates a highly efficient material.

Carbazole and its derivatives have attracted extensive interest because of their useful biological activity, and recently, they are expanding their applications as attractive building blocks for the construction of functional materials, such as photorefractive materials, photoconductors, nonlinear optical materials, light emitting materials, and hole-transporting materials, because of their inherent electron donating nature, excellent photoconductivity, and unique nonlinear optical property.^{24–27}

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Recently, we reported blue-LEP, which was composed with fluorene and alkoxy naphthalene, by the Suzuki coupling reaction.²⁸ The introduction of 1,5-dialkoxy naphthalene for the copolymerization with fluorene did not affect the oxidation potential and maximum emission wavelength of poly(fluorene), but it induced the distorted structure and suppressed intermolecular interaction. As a result, stable pure blue electroluminescence was observed. However, it showed the relatively low brightness.

In connection with the recent report,²⁸ we designed and synthesized the new copolymer, which is composed of dialkoxy naphthalene, *N*-alkylcarbazole, and fluorene. On the basis of copolymer of dialkoxy naphthalene and fluorene, the introduced carbazole unit can lead to tailor the energy level of polymer. Moreover, the carbazole unit can enhance the hole injection and the transporting ability of copolymer.

EXPERIMENTAL SECTION

Materials

All reagent and (Yongin City, Korea) solvents were purchased from Aldrich Chemical and Fluka (Seoul, Korea). Only analytical grade quality chemicals were used. PEDOT was purchased from Bayer (Seoul, Korea). Spectroscopic grade CHCl_3 (Aldrich Chemical Co., Yongin, Korea) was used for all absorption and emission experiments. All other compounds were used as received.

Synthesis

Synthesis of 2,6-dibromo-1,5-dihexyloxy naphthalene

The 2,6-dibromo-1,5-dihydroxynaphthalene (5 g, 15.7 mmol), 1-bromohexane (10.38 g, 63 mmol), NaI (0.94 g, 63 mmol), KOH (5 g, 15.7 mmol) was dissolved in ethanol.^{23,28} After the mixture was refluxed for 48 h, ethanol was evaporated. The mixture was extracted with ethyl acetate and^{23,28} washed with 10% aqueous NaOH and water. The crude product was separated by column chromatography with hexane as eluent. (25%) ¹H-NMR (500 MHz, CDCl_3) [ppm] δ 7.75 (m, 2H), 7.64 (m, 2H), 4.09 (s, 4H), 1.8 (m, 4H), 1.6 (m, 4H), 1.4 (m, 8H), 1.2 (m, 6H) FT-IR (KBr, cm^{-1}): 2950 (aliphatic C—H str), 3050 (aromatic C—H str), 1180 (aromatic C—Br str).

Synthesis of 9,9-dihexyl-2,7-di(1',2'-ethylborate) fluorene

The synthesis was followed by literature method.²⁸ ¹H-NMR (500 MHz, CDCl_3) [ppm] δ 7.8–7.7 (m, 6H), 4.43 (s, 8H), 2.0 (m, 4H), 1.2 (m, 12H), 0.75 (t, 6H), 0.58 (br s, 4H), FT-IR (KBr, cm^{-1}): 3053 (aromatic C—H str), 2964 (aliphatic C—H str), 1453 (B—O str).²⁸

Synthesis of 2,7-dibromo-9-(3,7-dimethyloctyl)-9H-carbazole

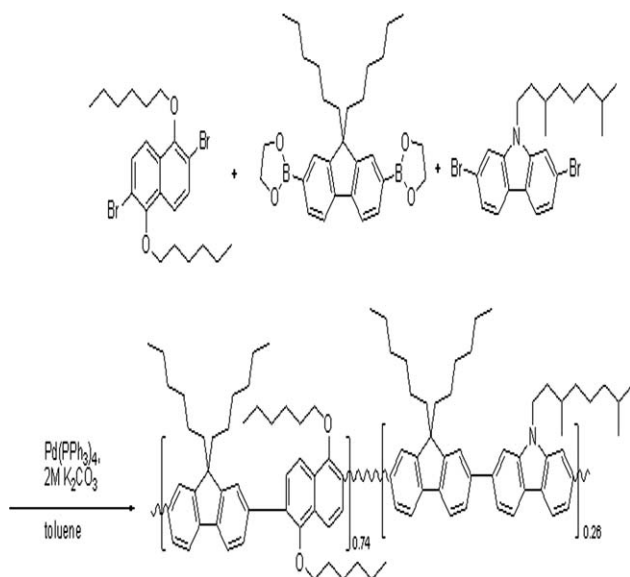
The synthesis was followed by literature method.²⁵ ¹H-NMR (500 MHz, CDCl_3) [ppm] δ 7.9 (s, 2H), 7.3–7.2 (m, 4H), 3.8 (t, 2H), 1.9 (m, 2H), 1.6–1.0 (m, 17H), FT-IR (KBr, cm^{-1}): 3053 (aromatic C—H str), 2964 (aliphatic C—H str), 1160 (Ar—Br str).

Polymer synthesis

The polymer was prepared from palladium catalyzed Suzuki coupling reaction. All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 9,9-dihexyl-2,7-di(1',2'-ethylborate) fluorene (1.786 mmol), 2,6-dibromo-1,5-dihexyloxy naphthalene (1.34 mmol), and 2,7-dibromo-9-(3,7-dimethyloctyl)-9H-carbazole (0.44 mmol) in 10 mL THF and 4 mL 2 M K_2CO_3 solution in water was added catalysts, $\text{Pd}(\text{PPh}_3)_4$ (8.4 mg, 0.6 mol%). The reaction mixture was heated at 80°C under nitrogen atmosphere for 8 h. Bromobenzene (0.05 g, 0.318 mmol) was added and then phenyl boronic acid (0.05 g, 0.41 mmol) was added with small amounts of catalysts for end-capping. After 2 h, the reaction mixture was poured into methanol (50 mL) and filtered with glass filter. The residue was dissolved in CHCl_3 and washed with water. After being dried over MgSO_4 , precipitation was twice repeated with chloroform/methanol. Yield = 70%.

INSTRUMENTS FOR CHARACTERIZATION

The ¹H NMR spectra were recorded with a Bruker AM-200 spectrometer. The FT-IR spectra were measured on a Bomem 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 polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (waters high-pressure GPC assembly Model M515 pump, u-Styrigel columns of HR4, HR4E, HR5E, with 500 and 100 Å, refractive index detectors, solvent THF).



Scheme 1 Synthetic scheme of new copolymer.

Cyclic voltammetry was carried out in a two-compartment cell with a model with platinum electrodes at a scan rate of 10 mV/sec against an Ag/Ag+ (0.1 M AgNO₃ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M Bu₄NBF₄ in acetonitrile.

FABRICATION OF THE LED

Poly(styrene sulfonate)-doped 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 isopropylalcohol sequentially. A thin polymer film (1000 Å) was spin-coated (3000 rpm, 50s) from a filtered (0.2 m filter) 1.0 wt % polymer solution in chlorobenzene on a PEDOT layer. A thin layer of LiF (5 Å) and subsequently 1500 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 method for the preparing polymer was outlined in Scheme 1. The mole ratio of copolymer using 9,9-dihexyl-2,7-di(1',2'-ethylborate) fluorene, 2,6-dibromo-1,5-dihexyloxy naphthalene and 2,7-dibromo-9-(3,7-dimethyloctyl)-9H-carbazole was 1 : 0.74 : 0.26. The preparation and purification of the polymer was carried out by Suzuki polymerization method as described in previous report.²⁸ The structure of the

obtained polymer was confirmed by ¹H-NMR and IR spectroscopies. Figure 1 portrayed the ¹H-NMR and IR spectra of copolymer. The obtained copolymer was highly soluble in most organic solvents such as chloroform, tetrahydrofuran, and toluene. The molecular weight of polymer was determined by GPC using polystyrene as standard and THF as eluent. The weight average molecular weight (M_w) of the polymer was 288,000 with a polydispersity index of 2.56. The thermal stability of the copolymer was evaluated by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurement under a nitrogen atmosphere because the material with high glass transition temperature as the active emissive layer can provide the device longevity. (Fig. 2) The

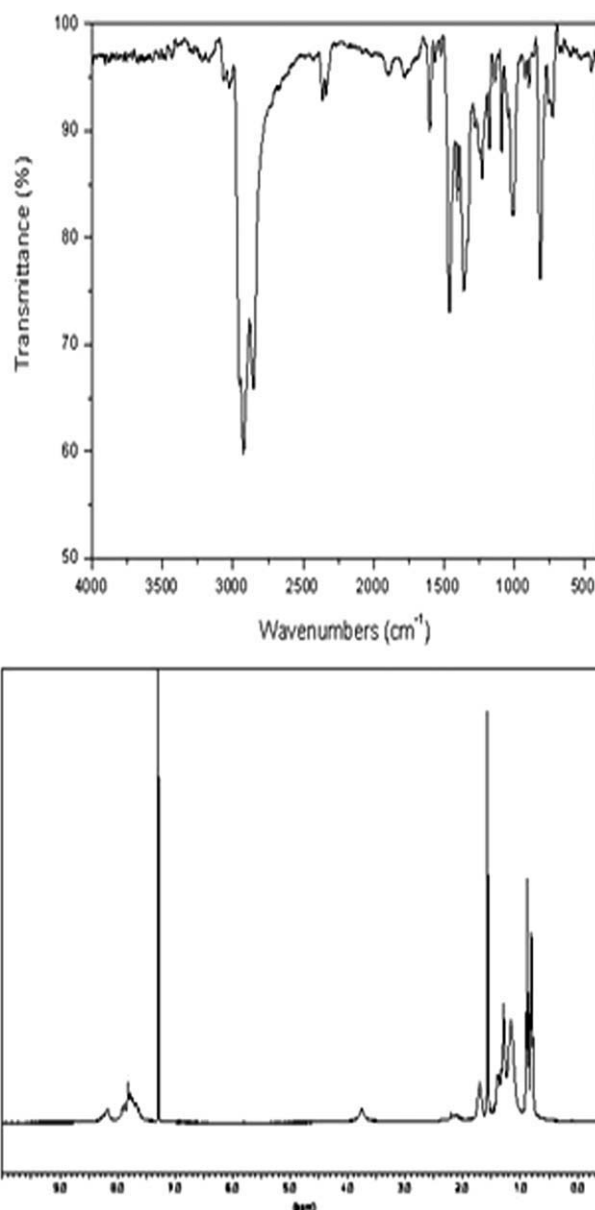


Figure 1 ¹H-NMR and IR spectra of new copolymer.

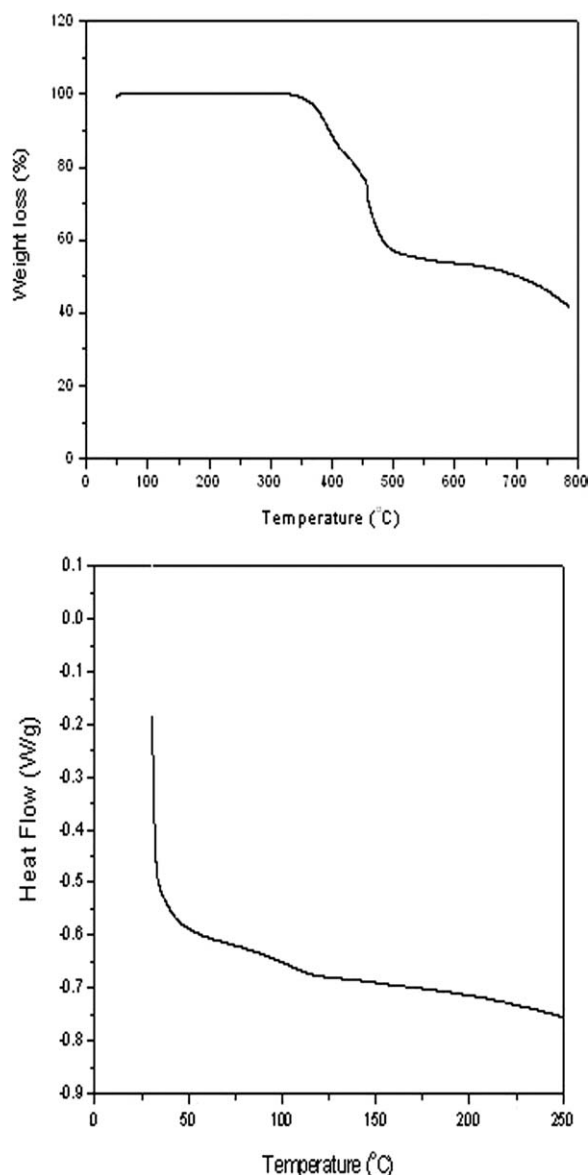


Figure 2 TGA and DSC thermograms of new copolymer.

copolymer was exhibit good thermal stability up to 378°C. The glass transition temperature (T_g) of copolymer showed at 108°C while the reported alternate copolymer containing 1,5-dihexyloxy naphthalene and 9,9-dihexyl fluorene with similar weight average molecular weight showed 126°C of glass transition temperature.²⁸ The decreased T_g may be attributed to the decrease of regularity due to randomly introduced *N*-(3,7-dimethyloctyl)carbazole comonomer. Figure 3 showed the optical absorption and photoluminescence spectra of a dilute solution of the polymer in chloroform. The maximum absorption of polymer showed at 370 nm, which was slightly red-shifted (4 nm) compared with reported alternate copolymer. The band-gap energy of the new polymer estimated from extrapolation of the low energy absorption spectra was

about 3.03 eV. The PL spectrum was recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the polymer. The polymer emitted strong blue fluorescence under ultraviolet irradiation both in a chloroform solution ($\lambda_{\text{max}} = 422$ nm) and in the film ($\lambda_{\text{max}} = 422$ nm), which was also red-shifted (17 nm) compared with reported alternate copolymer. From the results, it suggested that the randomly introduced (*N*-3,7-dimethyloctyl)carbazole comonomer affected optical properties of reported alternate copolymer.²⁸ The polymer has a PL quantum efficiency ($40 \pm 10\%$ using a dilute quinine sulfate solution as a standard).⁴⁻⁶

Cyclic voltammetry was performed on a film of polymer, calibrated against ferrocene-ferrocenium. The oxidation peak potentials of the obtained copolymer and reported alternate copolymer were measured to be $E_{\text{ox}} = 1.26$ V and 1.36 V, respectively. (Fig. 4) According to the results, it was supposed that the introduction of (*N*-3,7-dimethyloctyl)carbazole decreased the oxidation potential, implying easy hole injection as expected.

The PL spectra of copolymer before and after thermal annealing were studied at 100°C in the air for several hours. (Fig. 5) The PL spectra of polymer did not show any peak in the long wavelength region, which was generated from keto defect sites or aggregates/excimers even after annealing for 24 h at 100°C in air. From the result, it is suggested that the introduction of (*N*-3,7-dimethyloctyl)carbazole with effective hole injection does not affect polymer color purity, which is explained by distorted structure resulted from the steric interaction between the rigid

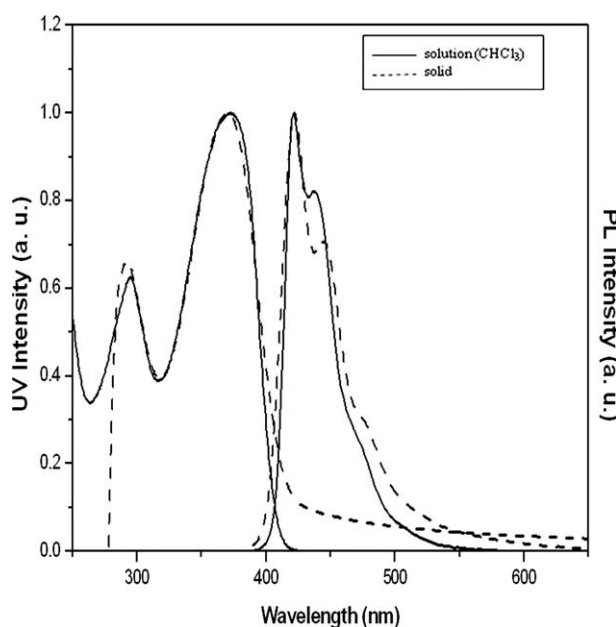


Figure 3 The optical absorption and photoluminescence spectra of copolymers in solution and film.

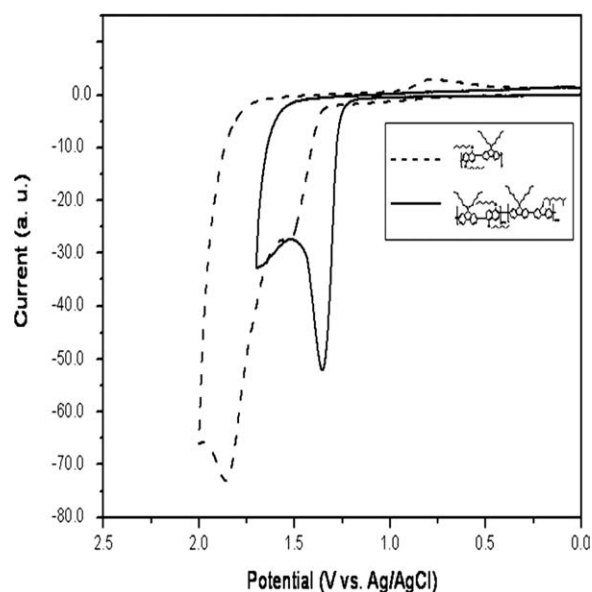


Figure 4 Cyclic voltammetry of reported alternating copolymer containing dihexyloxy naphthalene and dihexyl fluorene and obtained copolymer.

hexyloxy naphthalene unit and (9,9-dihexyl) fluorene unit or between (*N*-3,7-dimethyloctyl)carbazole unit and fluorene unit.

To investigate the electroluminescent property of the copolymer containing carbazole ITO/PEDOT/polymer/LiF/Al device was fabricated and evaluated. Figure 6 represented the voltage-current (*I*-*V*) and voltage-brightness curve (*L*-*V*) characteristics of device and the current and light arose at almost the same voltage (8.2 V). The maximum brightness of the device was 180 cd/m² and electroluminescent

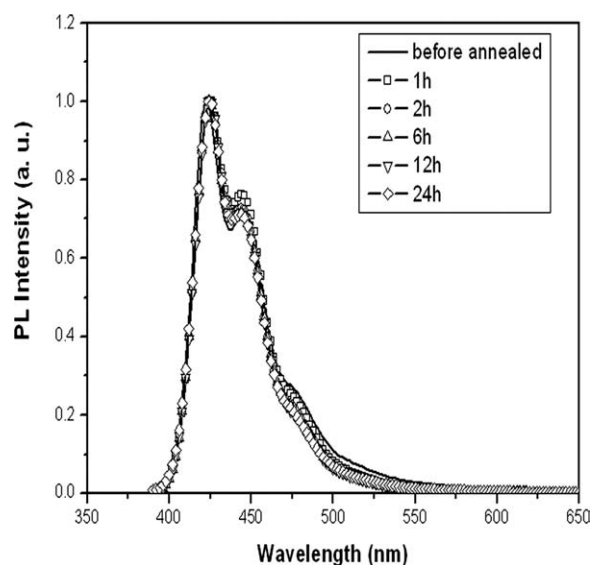


Figure 5 The PL spectra of copolymer before and after thermal annealing at 100°C in the air.

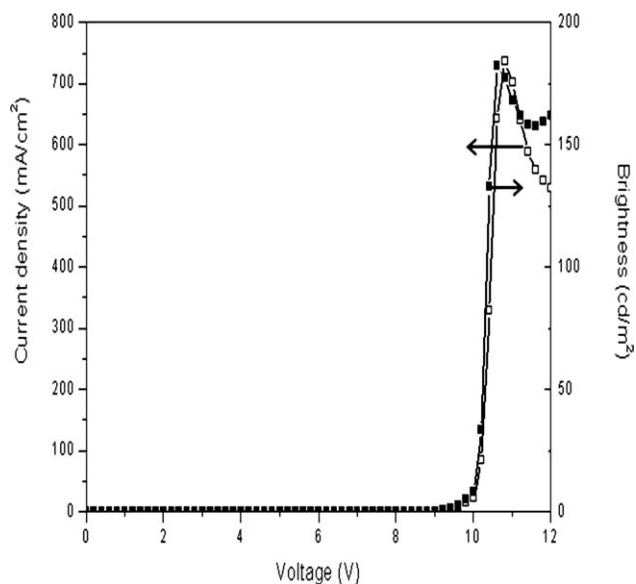


Figure 6 The current-voltage and luminescence-voltage characteristics of ITO/PEDOT/polymer/LiF/Al device.

efficiency of 0.04 cd/A was obtained. The increased brightness of device may be attributed to the increased hole injection and transporting. Figure 7 showed the electroluminescence spectrum, which displayed the maximum emission located at about 422 nm, indicating deep pure blue light emission. Also, the EL spectrum of polymer was consistent with PL spectrum. Based on the EL spectrum, the CIE (Commission Internationale de l'Éclairage) chromaticity coordinates was calculated to be ($x = 0.15$, $y = 0.12$).

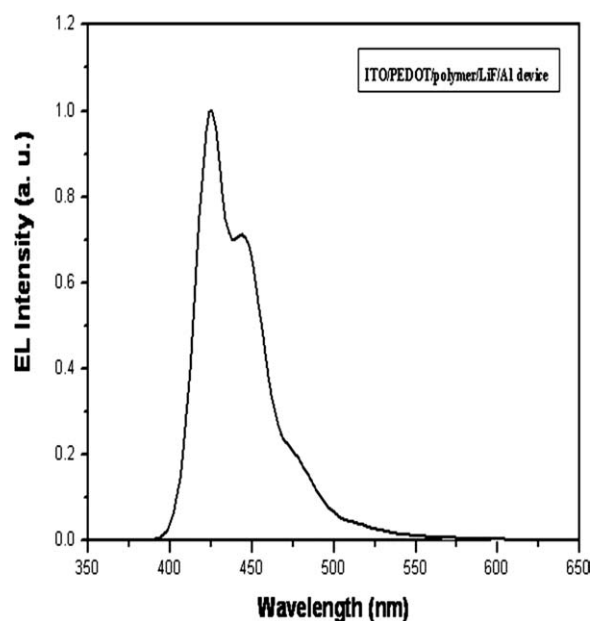


Figure 7 Electroluminescence spectrum of ITO/PEDOT/polymer/LiF/Al device.

CONCLUSION

We designed and synthesized the new copolymer, which was composed of dihexyloxy naphthalene, (*N*-3,7-dimethyloctyl)carbazole, and fluorene with mole ratio of 0.76 : 0.24 : 1. The randomly introduced (*N*-3,7-dimethyloctyl)carbazole affected energy level of copolymer due to easy hole injection as well as photophysical properties while it did not affect the distorted structure resulted from the steric interaction between the rigid hexyloxy naphthalene unit and fluorene unit or between (*N*-3,7-dimethyloctyl)carbazole unit and fluorene unit. The double-layered device with an ITO/PEDOT/polymer/LiF/Al structure has a maximum brightness of 180 cd/m² and pure blue EL emission ($\lambda_{\text{max}} = 422$ nm) with excellent CIE coordinates ($x = 0.15$, $y = 0.12$).

This work was supported by the Industrial Strategic Development Program [100035225, Development of core technology for high performance AMOLED on plastic] funded by MKE/KEIT.

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