Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 110–115
polymer
www.elsevier.com/locate/polymer

White-light-emitting diodes from single polymer systems based on polyfluorene copolymers end-capped with a dye

Po-I Lee, Steve Lien-Chung Hsu*, Rong-Fong Lee

Department of Materials Science and Engineering, National Cheng Kung University, 1 Ta-Hsueh Road, Tainan 701-01, Taiwan, ROC

Received 5 October 2006; received in revised form 9 November 2006; accepted 14 November 2006
Available online 4 December 2006

Abstract

New polymer white-light-emitting diodes from single polymer systems have been developed. The polymer systems were based on poly(fluorene-*co*-benzothiadiazole) backbones end-capped with a green-emission dye, *N*-phenyl-1,8-naphthalimide. By changing the molar ratio of these three units, the electroluminescence (EL) spectra can be adjusted to white-light emission with a structure of indium tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)/emission layer/Ca/Ag. The highest brightness in such a device configuration is 251 cd/m^2 at a current density of 400 A/m^2 with Commission Internationale de l'Eclairage (CIE) coordinates of (0.31,0.39). The EL spectra show color stability over different operating voltages.

Keywords: Polymer light-emitting diodes; White light; Copolymer

1. Introduction

White polymer light-emitting diodes (WPLEDs) have recently attracted great attention owing to their potential applications in back-lighting for liquid–crystal displays, full-color displays combined with a color filter, and next generation lighting sources, etc. [1–8]. Several approaches have been developed to reach WPLEDs. For example, using a polymer blending technique, such as blending red-, green-, and blue-light-emitting polymers or blending blue- and orange-light-emitting polymers [9–13]; and blending fluorescent or phosphorescent dyes into a polymer matrix, etc. [14–20]. However, there is a phase separation problem in these blending systems, which results in low efficiency and color instability of the WPLEDs. The white-light emitting from a single polymer system is considered as a promising approach to solve the phase separation problem encountered in blending systems [21–26].

In this work, we develop a new method to achieve white-light emission from a single polymer. A green-emission dye, *N*-phenyl-1,8-naphthalimide (NTI), was incorporated into a blue- and orange-light-emitting copolymer backbone, poly(fluorene-*co*-benzothiadiazole), by a end-capping approach. The molar ratio of these three composition units was adjusted to balance the light color and achieve white-light emission, but with the fluorene unit as the main part of the copolymer backbone.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were collected on a Brucker Advance 600 spectrometer. Molecular weight determination was carried out by using a Waters GPC 2414 in tetrahydrofuran (THF) via a calibration curve of polystyrene standards. Thermal stability was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) Q500 at a heating rate of 10 °C/min under nitrogen. The glass-transition temperature (T_g) was determined on a TA Instruments Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 20 °C/min under nitrogen.

---

* Corresponding author. Tel.: +886 6 2757575x62904; fax: +886 6 2346290.

E-mail address: lchsu@mail.ncku.edu.tw (S.L.-C. Hsu).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.11.026

Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. PL spectra were measured by a Hitachi F-4500 fluorescence spectrometer. EL spectra and luminance of the devices were measured using a Photoresearch PR650. The voltage–current was controlled by a Keithley 2400 power source. Cyclic voltammetry (CV) was carried out on a potentiostat/galvanostat model 283 (Princeton Applied Research) with a platinum electrode at a scan rate of 50 mV/s against Ag/AgCl reference electrode with nitrogen-saturated solution of 0.1 M tetra-*n*-butylammonium perchlorate $[CH_3(CH_2)_3]_4N\cdot ClO_4$ in acetonitrile.

2.2. Materials

2,7-Dibromo-9,9-dioctylfluore, 1,2-phenylenediamine, pyridine, thionyl chloride, hydrobromic acid, hydrogen peroxide solution, aniline, 4-bromo-1,8-naphthalic anhydride, 2,2-dipyridyl, 1,5-cyclooctadiene, bis(1,5-cyclooctadiene)nickel(0) $[Ni(COD)_2]$ were obtained from Aldrich. Toluene and *N*,*N*-dimethylformamide (DMF) were purchased from TEDIA, and distilled over calcium hydrate. Chloroform and acetic acid were also purchased from TEDIA and used as received.

2.3. Synthesis of monomers

2.3.1. 4,7-Dibromo-(2,1,3)-benzothiadiazole (DBBT)

The compound was prepared according to the literature [18] starting with 1,2-phenylenediamine. The yield was 73%; mp: 186 °C (lit. [18] 184–185 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.73 (s, 2H). Anal. Calcd for $C_6H_2N_2SBr_2$: C, 24.49; H, 0.68; N, 9.52. Found: C, 24.67; H, 0.77; N, 9.54.

2.3.2. N-Phenyl-4-bromo-1,8-naphthalimide (BrNTI)

4-Bromo-1,8-naphthalic anhydride (1 g, 3.6 mmol) was refluxed with aniline (0.37 g, 4 mmol) in 20 mL of acetic acid for 15 h. The solution was cooled to room temperature, and then poured into water. The precipitate was filtered and recrystallized from $CHCl_3$/methanol. The yield was 65%; mp: 231 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.66 (d, 1H), 8.56 (d, 1H), 8.42 (d, 1H), 8.03 (d, 1H), 7.84 (t, 1H), 7.48–7.55 (m, 3H), 7.25–7.32 (m, 2H). Anal. Calcd for $C_{18}H_{10}NO_2Br$: C, 67.36; H, 2.84; N, 3.98. Found: C, 61.14; H, 2.90; N, 3.86.

2.4. General procedures of copolymers' synthesis

All copolymers were synthesized in the same way. The pdof–2%BT–3%endNTI is taken as an example. To a 100 mL round bottom flask, $Ni(COD)_2$ (2 g, 7.11 mmol), 2,2-dipyridyl (1.11 g, 7.11 mmol) and 1,5-cyclooctadiene (0.768 g, 7.11 mmol) were dissolved in 10 mL of DMF under a nitrogen atmosphere. The solution was heated to 80 °C for half an hour to form a purple complex. 2,7-Dibromo-9,9-dioctylfluorene (1.67 g, 3.04 mmol), DBBT (0.019 g, 0.064 mmol) and BrNTI (0.034 g, 0.096 mmol) in 20 mL of toluene were added to the solution, and heated at 80 °C for 3 days. After being cooled to room temperature, the reaction mixture was poured into a mixture of 200 mL of HCl, 200 mL of acetone and 200 mL of methanol, which was stirred for 2 h. The precipitate was filtered, and redissolved in chloroform. Then it was precipitated in a large amount of methanol. The solid was dried in a vacuum oven at 70 °C overnight. The results of elemental analysis for each copolymer were used for the calculation of actual copolymer composition. Anal. Calcd for pdof–2%BT–3%endNTI: C, 89.22; H, 10.10. Found: C, 88.87; H, 10.36. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 (d, 2H), 7.70 (m, 4H), 2.12 (t, 4H), 1.14 (m, 24H), 0.85 (t, 6H).

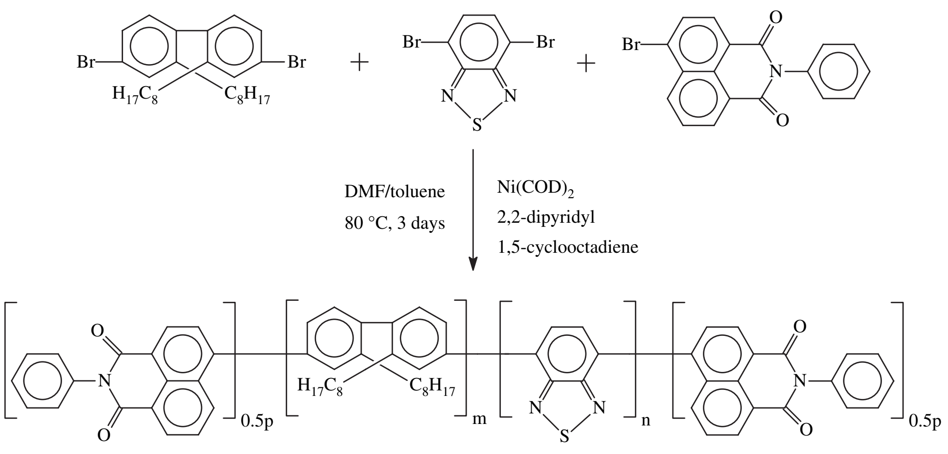
2.5. Light-emitting devices fabrication

The copolymer was dissolved in chloroform and filtered through a 0.45 μm filter. Patterned indium tin oxide (ITO) glass was cleaned with acetone, 2-propanol and deionized water in an ultrasonic bath, and dried on a hot plate at 120 °C. Then it was treated with O_2 plasma for 5 min before use. A 50 nm hole injection layer of poly(styrene sulfonic acid) doped poly(ethylene dioxythiophene) [PEDOT:PSS] (Baytron P CH 8000, Bayer AG, Germany) was spin-coated on the ITO, and subsequently baked for 10 min at 130 °C. On the top of it, the emitting polymer was spin-coated from its solution in chloroform. The thickness was about 120 nm. Finally, a thin layer of calcium (10 nm) was deposited by thermo-evaporation under a vacuum of 10^{-5} torr, and followed by a layer of silver (150 nm). The device testing was carried out in air at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of the copolymers

The synthetic route of the copolymers and the feed ratios of the co-monomers as well as the end-capper are shown in Scheme 1. The polymerization reactions were carried out via a Yamamoto polycondensation reaction with Ni(0) as the catalyst. The molar ratios of *N*-phenyl-1,8-naphthalimide (NTI) and benzothiadiazole (BT) in the copolymers were controlled in the range of 0.5–3 mol% and 3–2 mol%, respectively. The molecular weight, polydispersity and thermal properties of these copolymers are shown in Table 1. The weight-average molecular weights (Mw) of all copolymers are around 30,000 g/mol. The polydispersity indexes of these copolymers are typical for a polycondensation polymerization. The thermal stabilities of these copolymers were determined by thermogravimetric analysis (TGA) in nitrogen as shown in Fig. 1. All copolymers show good thermal stability because their decomposition temperatures (T_ds) are higher than 400 °C. The glass-transition temperatures (T_gs) of these copolymers were investigated by differential scanning calorimetry (DSC) under nitrogen. The T_gs of the copolymers are in the range of 83–92 °C. Due to the incorporation of rigid BT and NTI units into the backbone, the copolymers have higher T_gs than the pure polyfluorene, which has a T_g of 72 °C [27]. All copolymers are soluble in common organic solvents, such as chloroform, toluene and tetrahydrofuran (THF), which are able to undergo spin-coating process.



	molar ratio (%)
PF-2% BT-3% endNTI	m=95, n=2, p=3
PF-3% BT-2% endNTI	m=95, n=3, p=2
PF-2% BT-1% endNTI	m=97, n=2, p=1
PF-2% BT-0.5% endNTI	m=97.5, n=2, p=0.5

Scheme 1. Synthetic scheme for the copolymers.

Table 1
Weight-average molecular weights (Mw), polydispersity and thermal properties of the copolymers

Copolymer	Yield (%)	Mw ($\times10^{-4}$) g/mol	Polydispersity	T_g (°C)	T_d[a] (°C)
PF−2%BT−3%endNTI	82	3.4	2.2	92	421
PF−3%BT−2%endNTI	92	3.2	2.2	85	407
PF−2%BT−1%endNTI	87	2.9	2.5	85	409
PF−2%BT−0.5%endNTI	91	3.0	2.4	83	414

[a] Temperature of 5% weight loss measured by TGA in nitrogen.

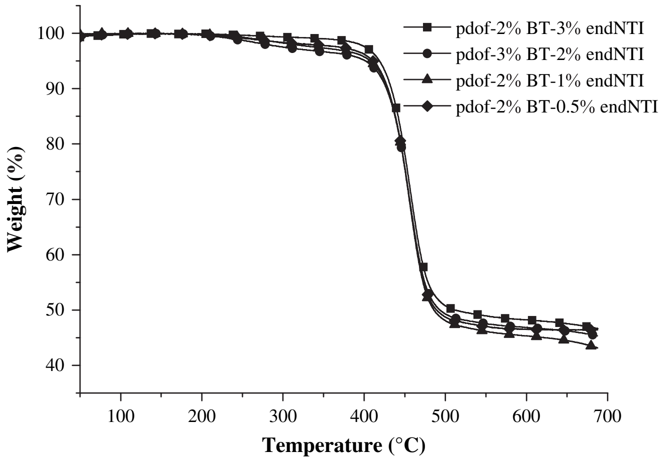


Fig. 1. TGA curves of the copolymers.

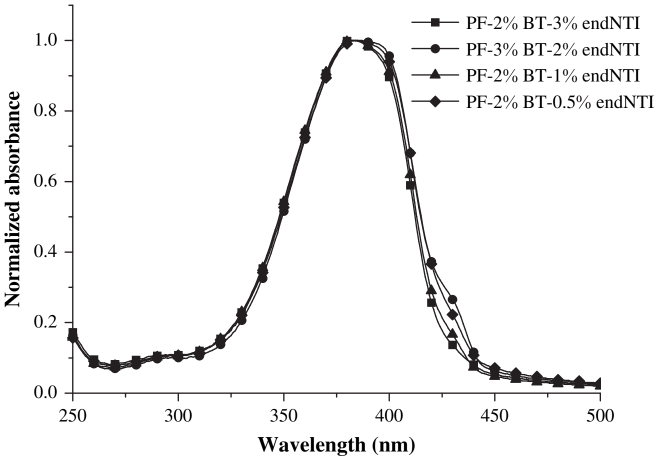


Fig. 2. UV−vis spectra of the copolymer films.

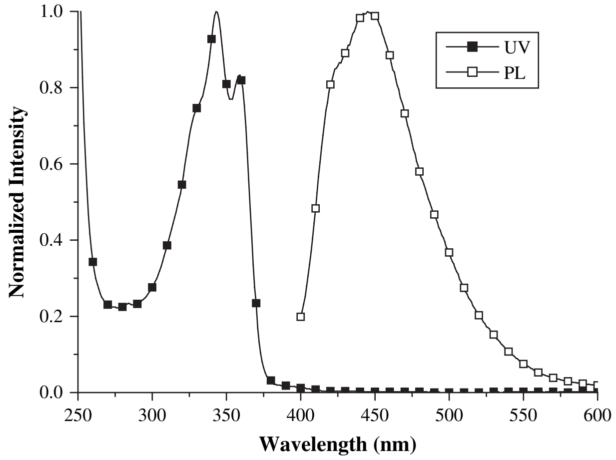


Fig. 3. PL and UV−vis spectra of the NTI dissolved in $CHCl_3$.

3.2. Optical properties

Fig. 2 is the absorption spectra of the copolymer films. The UV−vis spectra of the copolymers exhibit an absorption band at 380−390 nm, which is the peak of the fluorene units in the

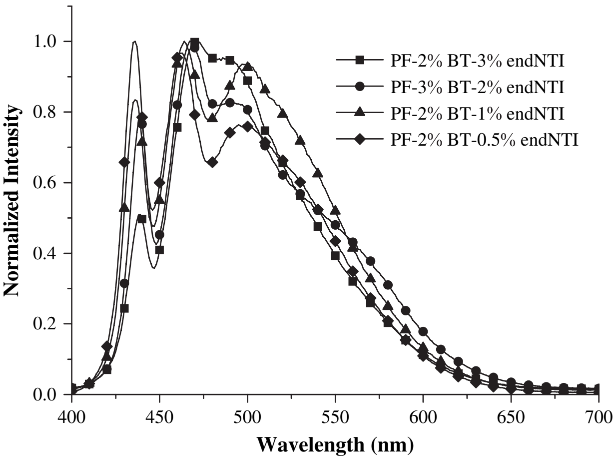


Fig. 4. PL spectra of copolymer films.

Table 2
Electrochemical properties of the copolymers

Copolymer	Oxidation potential (V vs FOC)	Reduction potential (V vs FOC)	HOMO (eV)	LUMO (eV)
PF−2%BT−3%endNTI	0.88	−2.33	−5.68	−2.47
PF−3%BT−2%endNTI	0.87	−2.35	−5.67	−2.45
PF−2%BT−1%endNTI	0.88	−2.36	−5.68	−2.44
PF−2%BT−0.5%endNTI	0.88	−2.37	−5.68	−2.43

$E_{\mathrm{FOC}} = 0.46$ V vs Ag/Ag^{+}; $E_{\mathrm{LUMO}} = -\exp(E_{\mathrm{red}}$ onset vs FOC + 4.8 V); $E_{\mathrm{HOMO}} = -\exp(E_{\mathrm{ox}}$ onset vs FOC + 4.8 V).

copolymers. The absorption band of the fluorene units is very intense, and overlaps the absorption peaks of the NTI units (340 and 360 nm), which are shown in Fig. 3. The absorption of the BT units is a weak peak at around 430 nm, because the BT content in the copolymers is small.

The photoluminescence (PL) spectra of the copolymers in the solid state are shown in Fig. 4. Two peaks (430 and 460 nm) are attributed to the emission of the fluorine units, and the emission of 500 nm is contributed by NTI units. The NTI unit is a fluorescent dye, and its PL spectrum in solution state is showed in Fig. 3. We incorporated the NTI unit into the copolymers by the end-capping method, and measured its PL spectrum in solid state. The emission was shifted from 450 to 500 nm. For the BT unit, when its content increases from 2 mol% to 3 mol%, a weak emission shoulder around 550 nm can be found. We can find that the intensity of the peak at 430 nm is higher while the contents of the BT and NTI units are reduced. According to the results, the energy transfer is more efficient from the fluorene units to the NTI units than to the BT units. The NTI unit can be considered as a fluorescent dopant in this system. Therefore, its PL contribution is greater than the poly(fluorene-*co*-benzothiadiazole) host.

The redox potentials of the copolymers were investigated by cyclic voltammetry (CV). The results are shown in Table 2.

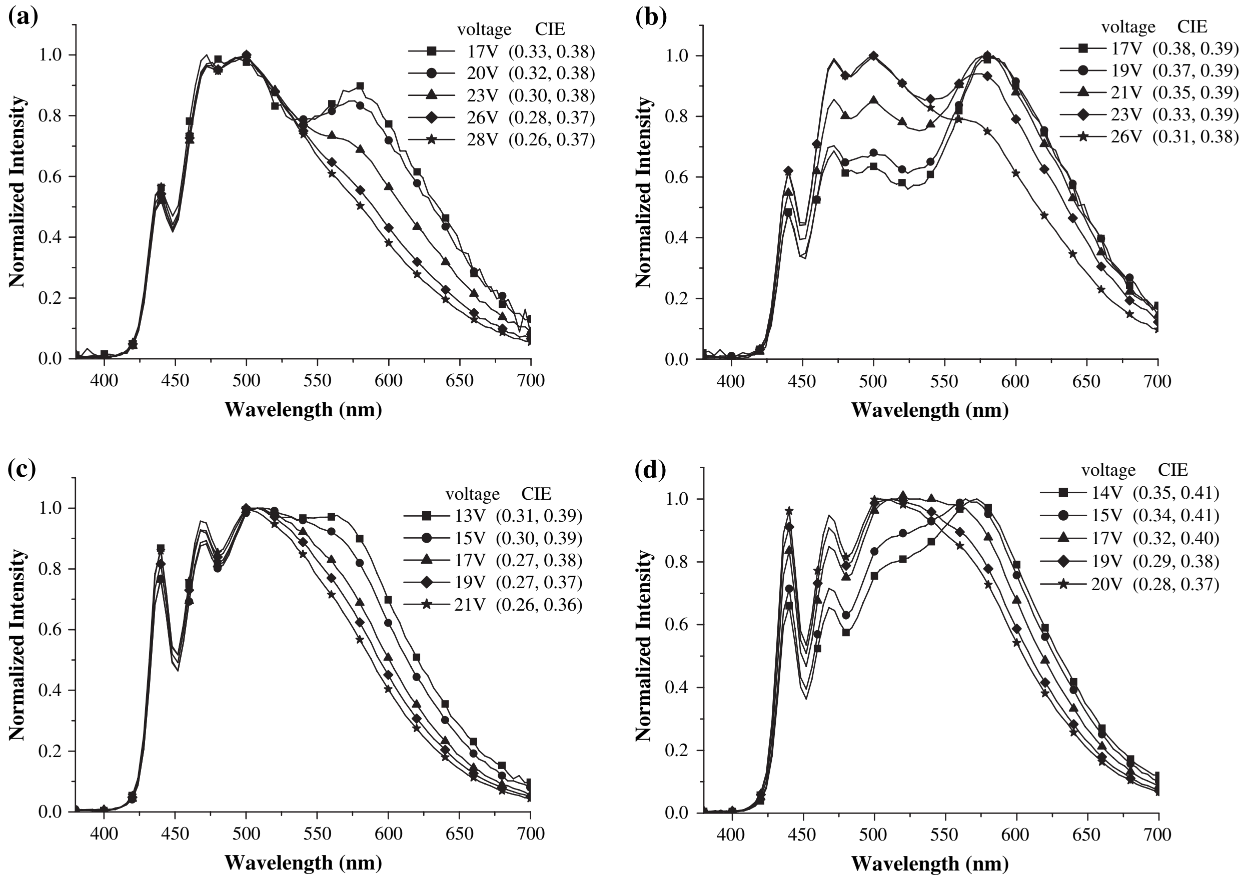


Fig. 5. EL spectra of devices from the copolymers: (a) PF−2%BT−3%endNTI, (b) PF−3%BT−2%endNTI, (c) PF−2%BT-1%endNTI, and (d) PF−2%BT−0.5%endNTI.

The electrochemical properties of the copolymers are similar to the pure polyfluorene. The results show that the contents of the BT and NTI units are too small to affect the LUMO and HOMO of the polyfluorene chain.

3.3. Electroluminescence (EL) properties of the devices

The structure of the WPLED devices is as follows: indium tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)/emission layer/Ca/Ag. Fig. 5 shows the EL spectra of the WPLEDs. The EL spectra of all copolymers exhibit a blue emission ($\lambda_{max} = 430$ nm/460 nm) from the fluorene units, a green emission ($\lambda_{max} = 500$ nm) from the NTI units, and an orange emission ($\lambda_{max} = 580$ nm) from the fluorene–BT copolymer units. It can be seen that the EL spectra are different from the PL spectra. In the PL spectra, the low PL intensity of orange emission is due to low PL efficiency of BT units and relatively high PL efficiency of NTI dye in PL spectrum. The peak intensity of orange emission in EL spectra is much larger than that in the PL spectra. This is due to charge-trapping mechanism in the EL process. There are more charges recombined on the BT units. The ratio of emission from the fluorene and NTI units increases with increasing current density. This is due to the partial saturation of emission from the BT units at high current density. When the bias is raised from low to high, the 1931 Commission Internationale de l'Eclairage (CIE) coordinates change from (0.33,0.38) to (0.26,0.37) for PF–2%BT–3%endNTI, from (0.38,0.39) to (0.31,0.38) for PF–3%BT–2%endNTI, from (0.31,0.39) to (0.26,0.36) for PF–2%BT–1%endNTI, and from (0.35,0.41) to (0.28,0.37) for PF–2%BT–0.5%endNTI. The white-light emission spectra of the copolymers studied in this work show color stability over different operating voltages, which is the major advantage of using the single polymer system. The current density (*I*)–voltage (*V*)–brightness (*B*) curves of the devices are shown in Fig. 6. The results indicate that the highest brightness in such a device configuration is 251 cd/m^2 at a current density of 400 A/m^2 with CIE coordinates of (0.31,0.39) for the copolymer of PF–2%BT–1%endNTI. The overall performance of the devices is summarized in Table 3. Further improvement of the performance in the devices could be attained by increasing the recombination of electrons and holes in the emission layer.

4. Conclusion

We have successfully synthesized single-polymer white-light-emitting systems by incorporating a green-emission dye

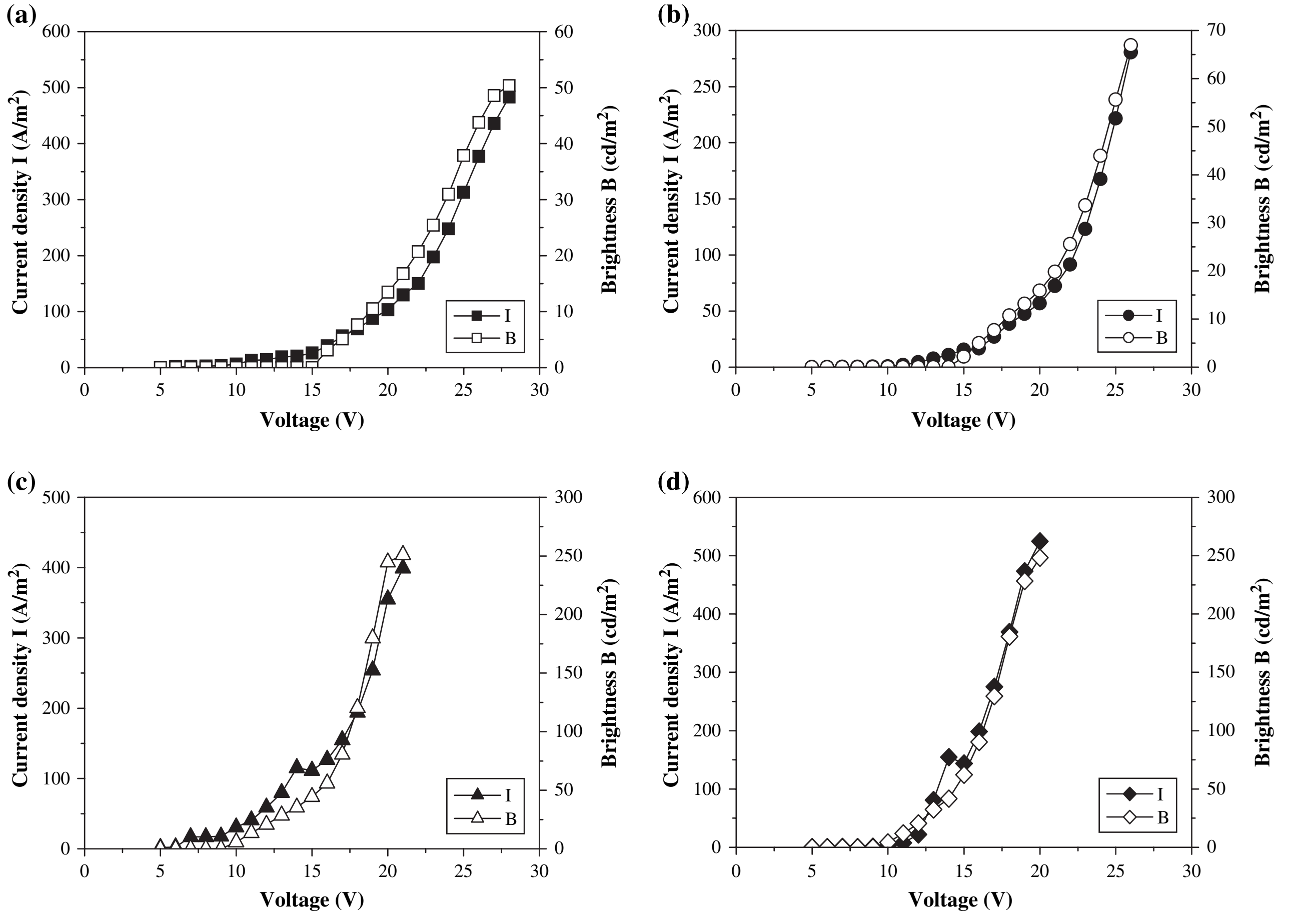


Fig. 6. Current density (*I*)–voltage (*V*)–brightness (*B*) curves of devices from the copolymers: (a) PF–2%BT–3%endNTI, (b) PF–3%BT–2%endNTI, (c) PF–2%BT–1%endNTI, and (d) PF–2%BT–0.5%endNTI.

Table 3
Performance of the copolymer devices

Copolymer	Bias[a] (V)	Current density[a] (A/m^2)	Luminance efficiency[a] (cd/A)	Maximum brightness (cd/m^2)	CIE (*x*,*y*)
PF–2%BT–3%endNTI	22	150	0.14	50	(0.32,0.38)
PF–3%BT–2%endNTI	20	57	0.28	67	(0.33,0.39)
PF–2%BT–1%endNTI	19	254	0.71	251	(0.31,0.39)
PF–2%BT–0.5%endNTI	18	369	0.49	248	(0.30,0.39)

[a] The devices were measured at the maximum luminance efficiency.

into a blue- and orange-light-emitting copolymer backbone through the end-capping approach. By changing the molar ratios of these monomer units, the EL spectra can be adjusted to white-light emission. The highest brightness in an EL device is 251 cd/m^2 at a current density of 400 A/m^2 with CIE coordinates of (0.31,0.39). The EL spectra show color stability over different operating voltages. The approach is proved to be a useful way to prepare efficient white-light-emitting diodes.

Acknowledgments

The financial support provided by the National Science Council (Taiwan, ROC) through project NSC95-2221-E-006-186 is greatly appreciated. The authors also thank the Center for Micro/Nano Technology Research, National Cheng Kung University, Tainan, Taiwan, for equipment access and technical support.

References

[1] Kido J, Shionya H, Nagai K. Appl Phys Lett 1995;67:2281.
[2] Strukelj M, Jordan RH, Dodabalapur A. J Am Chem Soc 1996;118:1213.
[3] Tasch S, List EJW, Ekstrom O, Graupner W, Leising G, Schlichting P, et al. Appl Phys Lett 1997;71:2883.
[4] Xie Z, Huang JS, Li CN, Wang Y, Li YQ, Shen J. Appl Phys Lett 1999;74:641.
[5] D'Andrade BW, Thompson ME, Forrest SR. Adv Mater 2002;14:147.
[6] Lee JI, Chu HY, Kim SH, Do LM, Zyung T, Hwang DH. Opt Mater 2002;21:205.
[7] Xu Y, Peng J, Mo Y, Hou Q, Cao Y. Appl Phys Lett 2005;86:163502.
[8] Tu G, Zhou Q, Cheng Y, Wang L, Ma D, Jing X, et al. Appl Phys Lett 2004;85:2172.
[9] Tokito S, Suzuki M, Sato F, Kamachi M, Shirane K. Org Electron 2003;4:105.
[10] Shih PI, Tseng YH, Wu FI, Dixit AK, Shu CF. Adv Funct Mater 2006;16:1582.
[11] Su HJ, Wu FI, Shu CF. Macromolecules 2004;37:7197.
[12] Hwang DH, Park MJ, Kim SK, Lee NH, Kim YB, Shim HK. J Mater Res 2004;19:2081.
[13] Huang J, Li G, Wu E, Xu Q, Yang Y. Adv Mater 2006;18:114.
[14] Kim T, Lee H, Park O, Chin B, Lee S, Kim J. Adv Funct Mater 2006;16:611.
[15] Tada K, Onodo M. Jpn J Appl Phys 2005;44:4167.
[16] Al Attar HA, Monkman AP, Tavasli M, Bettington S, Bryce MR. Appl Phys Lett 2005;86:121101.
[17] Gong X, Ma W, Ostrowski JC, Bazan GC, Moses D, Heeger AJ. Adv Mater 2004;16:615.
[18] Gong X, Moses D, Heeger AJ. J Phys Chem B 2004;108:8601.
[19] Kim JH, Herguth P, Kang MS, Jen KY, Tseng YH, Shu CF. Appl Phys Lett 2004;85:1116.
[20] Gong X, Wang S, Moses D, Bazan GC, Heeger AJ. Adv Mater 2005;17:2053.
[21] Furuta PT, Deng L, Garon S, Thompson ME, Frechet JMJ. J Am Chem Soc 2004;126:15388.
[22] Jiang J, Xu Y, Yang W, Guan R, Liu Z, Zhen H, et al. Adv Mater 2006;18:1769.
[23] Liu J, Zhou Q, Cheng Y, Geng Y, Wang L, Ma D, et al. Adv Funct Mater 2006;16:957.
[24] Tu G, Mei C, Zhou Q, Cheng Y, Geng Y, Wang L, et al. Adv Funct Mater 2006;16:101.
[25] Lee SK, Hwang DH, Jung BJ, Cho NS, Lee J, Lee JD, et al. Adv Funct Mater 2005;15:1647.
[26] Liu J, Zhou Q, Cheng Y, Geng Y, Wang L, Ma D, et al. Adv Mater 2005;17:2947.
[27] Yang W, Huang J, Liu C, Niu Y, Hou Q, Yang R, et al. Polymer 2004;45:865.