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High-Efficiency White-Light Emission from a Single Copolymer: Fluorescent Blue, Green, and Red Chromophores on a Conjugated Polymer Backbone**

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In recent years, white polymer light-emitting diodes (WPLEDs) have received great attention because of their potential application in full-color flat-panel displays and solid-state lighting. A variety of approaches have been proposed for the realization of white emission in PLEDs.[1] One of the successful approaches in small-molecule organic light-emitting diodes (OLEDs) fabricated by thermal deposition is to use a multilayer device system consisting of two or more active layers, where each layer emits a primary color.[2,3] The highest device performance in multilayer phosphorescent OLEDs reached external quantum efficiency (QE) and power efficiency of 18.7 % and 37.6 lm W^{-1}, respectively, at a luminance of 500 cd m^{-2} with Commission Internationale de L'Éclairage (CIE) coordinates of (0.40,0.41), as reported by the Forrest group.[4]

However, it is very difficult to fabricate multilayer PLEDs by solution processing because of the intermixing of different layers as a result of dissolution of the previously deposited layer. The most widely used approach for the manufacturing of PLEDs is to use the single-layer polymer blend system,[5–9] where the emitting layer consists of green and red emitters (small molecule or polymer) blended into a wide-gap blue-light-emitting polymer host and spin-coated onto an indium tin oxide/poly-(3,4-ethylenedioxythiophene) (ITO/PEDOT) substrate. Like most blended devices, the phase behavior of the guest and host is very sensitive to the driving voltage and the operating and shelf life; as a result, the color coordinates are not very stable.[5–7] Gong et al.[10] reported the first polymer multilayer white-light-emitting devices with a triplet phosphore doped into a blue-green polyfluorene host with water-soluble polyelectrolytes as the hole-transport layer (HTL) and electron-transfer layer (ETL). Recently, efforts have been made to prepare a single-component white polymeric emitter based on insufficient energy transfer, because phase segregation of chromophores can be significantly reduced by incorporating RGB (red–green–blue) chromophores into a single polymer chain. Lee et al. first reported a single fluorene-based copolymer composed of blue-, green-, and red-light-emitting units (although the RGB chromophores were not in full conjugation in the main chain) with a maximum brightness of 820 cd m^{-2} at 11 V with CIE coordinates of (0.33,0.35).[11] At almost the same time, Wang and co-workers adopted a slightly different synthetic strategy by which a green-emitting component was attached to the pendant chain and a red-emitting component was incorporated into the blue-emitting polyfluorene backbone.[12] The electroluminescent device exhibited a luminance efficiency of 1.59 cd A^{-1} and CIE coordinates of (0.31,0.34). A similar strategy with two chromophores for producing white-light-emitting polymers has been reported, with a luminous efficiency (LE) of 3.8 cd A^{-1} and CIE coordinates of (0.32,0.36),[13] and a luminous efficiency of 7.3 cd A^{-1} and CIE coordinates of (0.35,0.32).[14] Despite these efforts, the external quantum efficiency of WPLEDs remains much lower than that of a small-molecule WOLED fabricated by thermal deposition. It is noted that some efforts have been made to synthesize a single white-light-emitting small-molecule device[15] and to synthesize a white phosphorescent polymer that shows a slightly higher device efficiency of 4.7 cd A^{-1} with CIE coordinates of (0.38,0.35).[16]

This Communication proposes a novel strategy to realize white electroluminescence simultaneously with three primary color emission from a single conjugated copolymer with a backbone consisting of poly(9,9-dioctylfluorene) (PFO), 2,1,3-benzothiadiazole (BT), and 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole (DBT) as the blue-, green-, and red-light-emitting units, respectively. The difference between our copolymer and those reported by Lee et al.[11] and Liu et al.[12] is that it consists of a small amount of fluorescent red-emitting and green-emitting heterocyclic chromophores incorporated in full conjugation with a blue-emitting polymer backbone (Scheme 1). By incorporating a very small controlled amount of green and red chromophores into the blue host main chain, we achieved sufficient isolation of red and green chromophores along the blue-emitting main chain, leading to incomplete energy transfer not only from blue to green and red, but also the possibili-

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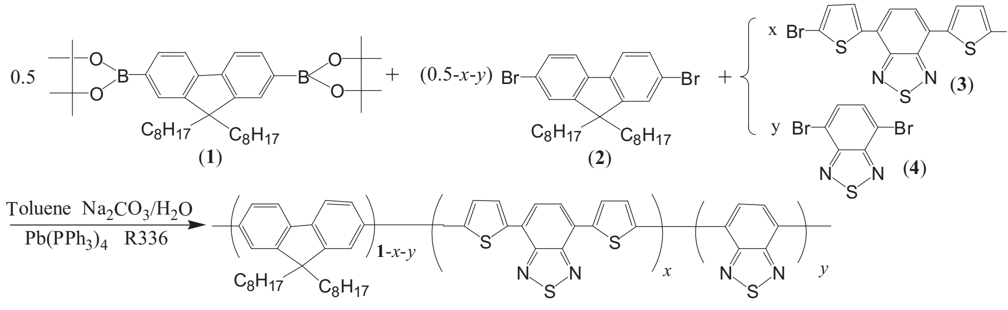

PFO-DBT$_x$-BT$_y$

	feed ratio
PFO-R005	x=0.00005, y=0
PFO-R005-G010	x=0.00005, y=0.00010
PFO-R010-G018	x=0.00010, y=0.00018
PFO-R015-G025	x=0.00015, y=0.00025

Scheme 1. Chemical structures and synthetic route for the formation of the copolymers.

ty of control of the energy transfer from green to red. A broad white electroluminescence with three distinguishable emission peaks at 452, 524, and 616 nm, is successfully achieved from a single-layer device of a single copolymer. The relative intensities of these three emissions vary according to the relative compositions of the corresponding chromophores. The optimized composition of RGB chromophores on the single polymer chain results in high-efficiency pure white-light emission. The external quantum and luminance efficiency reached 3.84 % (photon/electron (ph/el)) and 6.20 cd A^{-1}, respectively, with CIE coordinates of (0.35,0.34), which are very close to the CIE coordinates for National Television System Committee (NTSC) standard white-light emission (0.33,0.33).

The chemical structure and the synthetic route to the new copolymer are shown in Scheme 1. PFO was chosen as the blue-light-emitting polymer, with BT and DBT as the green- and red-light-emitting units, respectively.[17–19] We have previously reported that in the copolymer PFO-DBT, a full-energy transfer in the PFO-DBT devices is observed when the DBT content is equal to or greater than 0.05 mol % relative to the fluorene unit.[18] A similar situation was observed for PFO-BT copolymers. In order to achieve balanced RGB emission by incomplete energy transfer, four different copolymers with DBT and BT molar contents less than 0.05 % were synthesized and investigated: PFO-R005 with 0.005 % DBT incorporated into PFO; PFO-R005-G010 with 0.005 % DBT and 0.01 % BT; PFO-R010-G018 with 0.01 % DBT and 0.018 % BT; and PFO-R015-G025 with 0.015 % DBT and 0.025 % BT (Scheme 1). As shown below, adding 0.01 % DBT and 0.018 % BT to the PFO main chain achieves the best result in terms of a red–green–blue emission balance. We note that, because of the extremely low dopant content (less than 0.05 mol %) in the polymer main chain, it is almost impossible to determine an actual composition of the copolymers. Based on comparative studies of the initial monomer feed ratio and the elemental analysis of the resulting copolymers with higher heterocycle content in our previous studies,[16,17,19–22] it is natural to postulate that the actual composition of copolymers with a very small heterocycle content is also very close to the feed ratio.

The UV absorption of the copolymer PFO-R005 (others are identical and therefore omitted here) and photoluminescence (PL) spectra of the four different copolymers in solid films are shown in Figure 1a. It can be seen that the absorption spectra of the copolymers are practically identical to those of

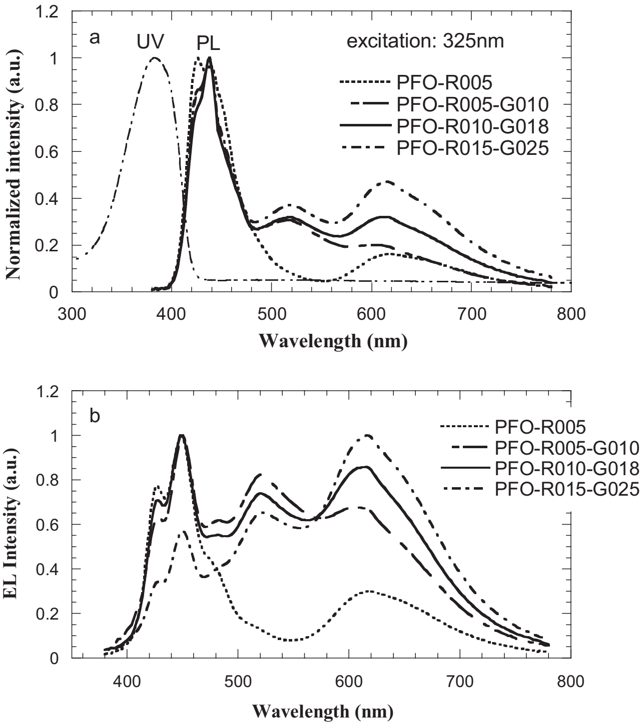

Figure 1. a) UV absorption and PL spectra of the copolymers. b) Electroluminescence (EL) spectra of the devices made from these copolymers with device configurations ITO/PEDOT/PVK/PFO-BT-DBT/Ba/Al at a current density of 13.3 mA cm^{-2}. PVK: poly(vinylcarbazole).

the PFO homopolymer[17,19] because of the very low content of DBT and BT units. In the PL spectra of the copolymers (Fig. 1), PFO-R005 shows two emissions peaks at 426 and 618 nm, attributed to the PFO and DBT units in the copolymer. PFO-R005-G010, PFO-R010-G018, and PFO-R015-G025 copolymers show three emission peaks, which cover a wide range of the visible region, and the intensities of the green- and red-emission bands increases with increasing amount of green- and red-light-emitting units in the copolymer. From our previous studies,[16–19] the three distinguishable PL peaks of the copolymers PFO-R005-G010, PFO-R010-G018, and PFO-R015-G025 can be attributed to the individual emissions originating from the three chromophores (PFO, DBT, and BT) as a result of the incomplete energy transfer from the blue-emitting unit to the green- and red-emitting units. The PL quantum efficiencies of copolymers with small BT and DBT content (< 0.05 %) measured in the integrating sphere under 325 nm excitation (He:Cd laser) increased up to 60 % (Table 1) with increasing BT and DBT content, compared to 47 % for PFO homopolymers.[17] This fact indicates that incorporation of an extremely low content (< 0.05 %) of BT and DBT chromophores in the polymer backbone reduces the interchain interaction of polyfluorene chains, resulting in less concentration quenching and higher PL efficiency.[17]

In order to investigate the electroluminescence properties of the copolymers, light-emitting diodes were made up with the following device structure: ITO/PEDOT (50 nm)/PVK (40 nm)/PFO-BT-DBT (75 nm)/Ba/Al, where poly(vinylcarbazole) (PVK) acts as a HTL. The device performances are listed in Table 1. The electroluminescence (EL) spectra of the devices from different copolymers are shown in Figure 1b. It can be seen that the EL spectra of the copolymers show three balanced blue-, green-, and red-emissions peaks at 438, 516, and 604 nm, and 438, 518, and 616 nm, for the devices manufactured from PFO-R005-G010 and PFO-R010-G018 copolymers, respectively. The CIE coordinates of (0.32,0.34) and (0.34,0.33) of these EL emissions with full width at half maximum (FWHM) of 230 and 250 nm, are very close to those of pure white light (0.33,0.33). The PFO-R015-G025 copolymer with increased BT and DBT content showed emissions at 520 and 616 nm exhibiting a much greater intensity of green and red peaks than blue PFO emission, resulting in CIE coordinates of (0.40,0.37). Comparing PL (Fig. 1a) and EL (Fig. 1b) spectra, we note that the relative intensity of green (BT unit) and red (DBT unit) peaks in the EL spectra is significantly higher than that of the PL peaks of the same polymer composition. It seems that, except for the energy transfer process from PFO to the BT and DBT units, direct charge trapping might play an important role in the EL process, resulting in enhanced green and red emission.

White-emitting devices from the single component copolymer show very good current stability. Figure 2 compares EL spectra of the device from the PFO-R010-G018 copolymer at different operating voltages. The CIE coordinates show no dramatic change: (0.34,0.32), (0.33,0.31), (0.31,0.30), (0.31,0.30), and (0.31,0.31) at driving voltages of 9, 10, 12, 14, and 16 V, respectively, with brightnesses of 416, 896, 2476, 5167, and 6994 cd m^{-2}. These results indicate that the WPLEDs from the PFO-R010-G018 copolymer are quite stable, even at a high luminance of nearly 7000 cd m^{-2}. The enhanced stability of the white emission of a single component copolymer is obviously due to the sufficient isolation of green and red chromophores incorporated into the polymer backbone, which restricts change of the energy transfer from green to red chromophores under a high current density. As a result, the relative intensities of three distinguishable RGB primary emissions, which constitute a broad white emission, remain stable.

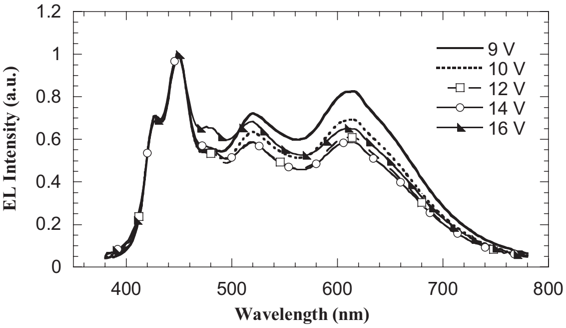

Figure 2. EL spectra of the devices with the PFO-R010-G018 copolymer at voltages varying from 9 to 16 V.

Recently, heat treatment has often been used to effectively increase the efficiency of the PLED.[23,24] Heat treatment of a polymeric thin film affects the PLED not only by improvement of interfacial adhesion[23] but also by the change of the intrinsic properties of the organic film itself.[25] Higher brightness and higher external electroluminescent quantum efficiency could be achieved this way, as reported respectively by Han,[26] Niu,[24] and Park.[23] Herein, after spin-coating, heat treatment of emissive layers at annealing temper-

Table 1. Performance of devices based on different copolymers (ITO/PEDOT(50 nm)/PVK(40 nm)/PFO-BT-DBT(75 nm)/Ba/Al).

Copolymer	Voltage [V]	Current density [mA cm^{-2}]	Luminance [cd m^{-2}]	QE [%]	LE [cd A^{-1}]	CIE [a] (x,y)	QE(PL) [b] [%]
PFO-R005	7.92	12.9	241.60	1.35	1.87	(0.25,0.17)	50.30
PFO-R005-G010	8.88	15.9	472.77	1.84	2.97	(0.32,0.34)	55.38
PFO-R010-G018	8.64	15.6	534.44	2.13	3.43	(0.34,0.33)	57.00
PFO-R015-G025	9.36	14.5	475.20	2.20	3.27	(0.40,0.37)	62.28

[a] Obtained at a current density of 13.3 mA cm^{-2}. [b] Photoluminescence quantum efficiency obtained under 375 nm excitation.

atures from 120 to 180 °C for 10 min was performed for the white-light-emitting devices based on the PFO-R010-G018 copolymer. The performances of the devices are listed in Table 2. The EL spectra of these devices are shown in Figure 3. The maximum optical output tended to increase as the annealing temperature increased, and the best performance, with an external quantum efficiency of 3.84 % (ph/el), luminance efficiency of 6.20 cd A^{-1}, and CIE coordinates of (0.35,0.34), was achieved after annealing for 10 min at 150 °C (Fig. 4).

Figure 5 compares atomic force microscopy (AFM) images of the copolymer (PFO-R010-G018) film before and after heat treatment. AFM images of PFO-R010-G018 film show that the surface roughness root mean square (rms) increases from 0.987 nm for the pristine film (Fig. 5a) to 2.114 nm after a 10 min heat treatment at 150 °C on the 1 μm scale (Fig. 5b). The fact that the X-ray diffraction pattern of PFO-R010-G018 films before and after heat treatment at 150 °C does not show any difference (only the same broad diffraction band attributed to the amorphous polymer can be observed) and that the thermal treatment of devices from annealed PFO-R010-G018 films after cathode deposition does not cause a further improvement in device performance, suggests that more effective electron injection after thermal treatment is associated with the increased contact area between the emissive layer and the Ba/Al cathode.

In conclusion, we have obtained high-efficiency white-light emission from a single copolymer with three emissive units (PFO, BT, DBT) in a conjugated polymer backbone. The electroluminescent device fabricated from the PFO-R010-G018 copolymer exhibited the best performance, with an external quantum efficiency of 3.84 % (ph/el), luminance efficiency of 6.20 cd A^{-1}, and CIE coordinates of (0.35,0.34) after annealing for 10 min at a temperature of 150 °C. Moreover, the color coordinates of the resulting white-light emission remained extremely stable over a wide range of driving voltages. Incomplete energy transfer from the blue polyfluorene backbone to the green and red units, and restricted energy transfer from the green to red chromophores due to sufficient isolation of these units along the conjugated backbones, led to three distinguishable primary emissions, thereby giving a broad white emission of balanced RGB components with perfect CIE coordinates.

Table 2. Performance of annealed devices based on PFO-R010-G018 copolymers (ITO/PEDOT(50 nm)/PVK(40 nm)/PFO-R010-G018(75 nm)/Ba/Al).

Temperature [a] [°C]	Voltage [V]	Current density [mA cm^{-2}]	Luminance [cd m^{-2}]	QE [%]	LE [cd A^{-1}]	CIE [b] (x,y)
No treatment	7.24	9.13	428	2.92	4.70	(0.32,0.31)
120	8.26	72.7	3911	3.34	5.39	(0.34,0.32)
135	7.20	10.7	609	3.52	5.67	(0.34,0.32)
150	7.20	10.5	654	3.84	6.20	(0.35,0.34)
180	8.08	66.9	3354	3.11	5.01	(0.38,0.36)

[a] Annealed for 10 min. [b] Obtained at a current density of 13.3 mA cm^{-2}.

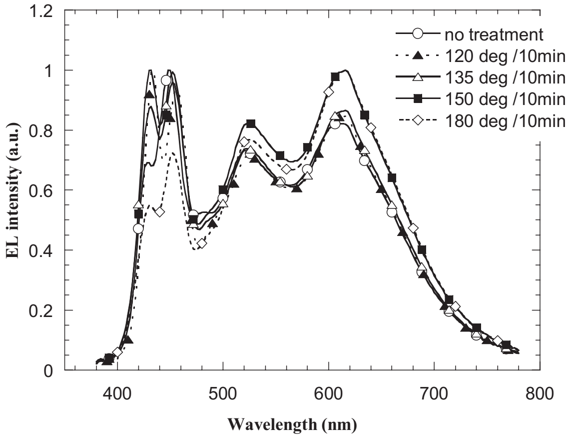

Figure 3. EL spectra of the white-EL device with different thermal treatments.

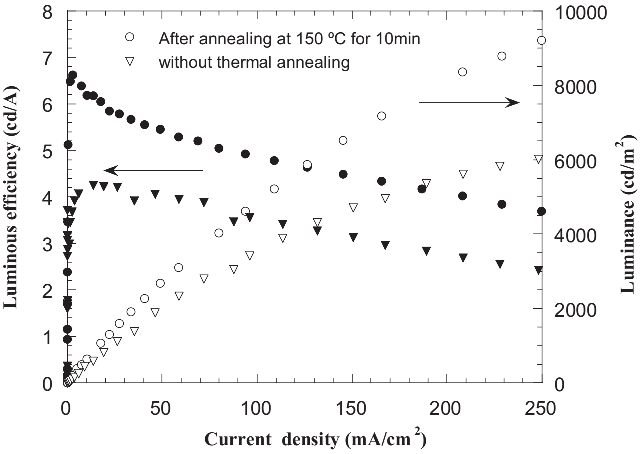

Figure 4. Luminous efficiency and light output versus the current density of devices manufactured from the copolymer PFO-R010-G018 film with and without thermal treatment (at 150 °C for 10 min) before cathode deposition.

Experimental

The compounds used in this study, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**1**), 2,7-dibromo-9,9-dioctylfluorene (**2**), 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**3**), and 4,7-dibromo-2,1,3-benzothiadiazole (**4**), were synthesized according to the procedure described in our previous studies [17,19–22].

Synthesis of the Copolymers: **1**, **2**, **3** (1.0×10^{-5} mol L^{-1} solution in toluene), **4** (2.0×10^{-5} mol L^{-1} solution in toluene), $(PPh_3)_4Pd^0$ (0.5–1 mol %), and Aliquat 336 were dissolved in a mixture of toluene and an aqueous solution of 2 M Na_2CO_3. The solution was refluxed for 24 h while being stirred vigorously in an argon atmosphere. Bromobenzene and **1** were subsequently added to end-cap the polymer chain. The whole mixture was poured into methanol. The precipitate was filtered off, washed with acetone, and purified by column chromatography (silica gel, toluene; yield: 80–90 %). Although the content of narrow band-gap (NBG) units 4,7-bis(2-thienyl)-2,1,3-

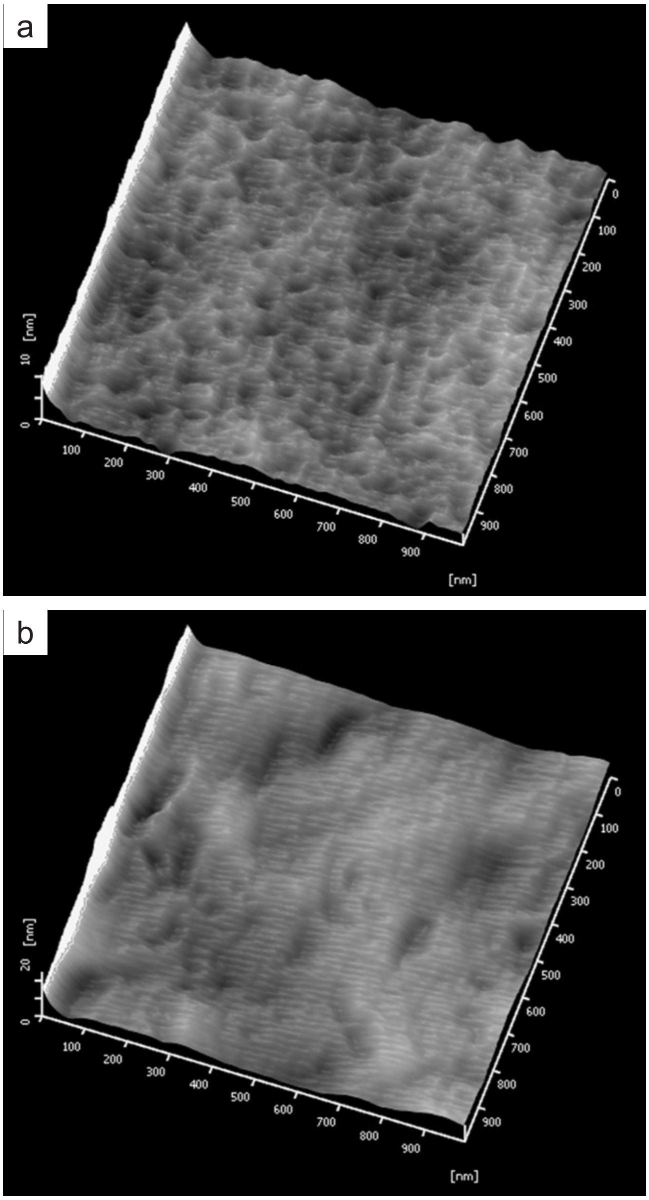

Figure 5. AFM images (1 µm × 1 µm scale) of the PFO-R005-G010 copolymer film a) before and b) after heat treatment at 150 °C for 10 min.

benzothiadiazole (DBT) and 2,1,3-benzothiadiazole (BT) in the copolymers is too low to be detected by ^{1}H NMR and elemental analysis, the actual ratios of DBT and BT can be assumed to be equal to the feed ratios.

Device Fabrication and Instruments: Polymers were dissolved in toluene or *p*-xylene and filtered through a 0.45 µm filter. Indium tin oxide (ITO; ca. 15 Ω per square) substrates were cleaned by a routine cleaning procedure that included sonication in detergent followed by repeated sonication in distilled water, acetone, and isopropyl alcohol. After treatment with oxygen plasma, 50 nm of poly-(3,4-ethylenedioxythiophene)-poly(styrenesulfonic acid) (PEDOT:PSS) (Baytron P 4083, Bayer AG) used as a hole-injection layer at the anode interface was spin-coated onto the ITO substrate, and then dried in a vacuum oven at 80 °C for 8 h. Poly(vinylcarbazole) (PVK; Aldrich) from 1,1,2,2-tetrachloroethane solution was subsequently coated on top of a dried PEDOT:PSS layer. A thin film of electroluminescent copolymer was coated onto the anode by spin-casting inside a nitrogen-filled drybox (Vacuum Atmospheres). The film thickness of the active layers was around 75 nm, as measured with an Alfa Step 500 surface profiler (Tencor). A thin layer of Ba (3–4 nm) and subsequently 200 nm layers of Al were evaporated on the top of an electroluminescent polymer layer under a vacuum of 1×10^{-4} Pa. Device performances were measured inside a drybox (Vacuum Atmospheres). Current–voltage (*I–V*) characteristics were recorded with a Keithley 236 source meter. The luminance of the device was measured with a calibrated photodiode. The external quantum efficiency was verified by measurement in the integrating sphere (IS-080, Labsphere), and luminance was calibrated by using a PR-705 SpectraScan spectrophotometer (Photo Research) after encapsulation of the devices with UV curing epoxy and a thin cover glass. The PL and EL spectra of the copolymer were studied with a PR-705 SpectraScan spectrophotometer.

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[1] B. W. D'Andrade, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 1585.
[2] R. H. Jordan, A. Dodabalapur, M. Strukelj, T. M. Miller, *Appl. Phys. Lett.* **1996**, *68*, 1192.
[3] Y. Z. Wang, R. G. Sun, F. Meghdadi, G. Leising, A. J. Epstein, *Appl. Phys. Lett.* **1999**, *74*, 3613.
[4] Y. R. Sun, N. C. Giebink, H. Kanno, B. W. Ma, M. E. Thompson, S. R. Forrest, *Nature* **2006**, *440*, 908.
[5] J. Kido, H. Shionoya, K. Nagai, *Appl. Phys. Lett.* **1995**, *67*, 2281.
[6] S. Tasch, E. J. W. List, O. Okström, W. Graupner, G. Leising, P. Schlichting, U. Rohr, Y. Geerts, U. Scherf, K. Müllen, *Appl. Phys. Lett.* **1997**, *71*, 2883.
[7] M. Granström, O. Inganäs, *Appl. Phys. Lett.* **1996**, *68*, 147.
[8] X. Gong, W. Ma, J. C. Ostrowski, G. C. Bazan, D. Moses, A. J. Heeger, *Adv. Mater.* **2004**, *16*, 615.
[9] X. Gong, D. Moses, A. J. Heeger, S. Xiao, *J. Phys. Chem. B* **2004**, *108*, 8601.
[10] X. Gong, S. Wang, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2005**, *17*, 2053.
[11] S. K. Lee, D. H. Hwang, B. J. Jung, N. S. Cho, J. Lee, J. D. Lee, H. K. Shim, *Adv. Funct. Mater.* **2005**, *15*, 1647.
[12] J. Liu, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Adv. Mater.* **2005**, *17*, 2974.
[13] G. L. Tu, C. Y. Mei, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Adv. Funct. Mater.* **2006**, *16*, 101.
[14] J. Liu, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Adv. Funct. Mater.* **2006**, *16*, 957.
[15] J. Y. Li, D. Liu, C. W. Ma, O. Lengyel, C. S. Lee, C. H. Tung, S. T. Lee, *Adv. Mater.* **2004**, *16*, 1538.
[16] J. X. Jiang, Y. H. Xu, W. Yang, R. Guan, Z. Q. Liu, H. Y. Zhen, Y. Cao, *Adv. Mater.* **2006**, *18*, 1769.
[17] Q. Hou, Y. Xu, W. Yang, M. Yuan, J. Peng, Y. Cao, *J. Mater. Chem.* **2002**, *12*, 2887.
[18] J. Luo, J. B. Peng, Y. Cao, Q. Hou, *Appl. Phys. Lett.* **2005**, *87*, 261 103.
[19] R. Q. Yang, R. Y. Tian, Q. Hou, W. Yang, Y. Cao, *Macromolecules* **2003**, *36*, 7453.
[20] X. Li, Y. Zhang, R. Yang, J. Huang, W. Yang, Y. Cao, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2325.
[21] X. Li, W. Zeng, Y. Zhang, Q. Hou, W. Yang, Y. Cao, *Eur. Polym. J.* **2005**, *41*, 2923.
[22] F. Hang, L. Hou, H. Wu, X. Wang, H. Shen, W. Cao, W. Yang, Y. Cao, *J. Am. Chem. Soc.* **2004**, *126*, 9845.
[23] T. W. Lee, O. O. Park, *Adv. Mater.* **2000**, *12*, 801.
[24] Y. H. Niu, Q. Hou, Y. Cao, *Appl. Phys. Lett.* **2002**, *81*, 634.
[25] T. Kreouzis, D. D. C. Bradley, A. J. Campbell, *Proc. SPIE* **2004**, *5214*, 197.
[26] T. Ahn, H. Lee, S. H. Han, *Appl. Phys. Lett.* **2002**, *80*, 392.