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A soluble self-doped conducting polyaniline graft copolymer as a hole injection layer in polymer light-emitting diodes

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Abstract

We demonstrate that a novel soluble self-doped conducting polyaniline graft copolymer can be used for a hole injection layer (HIL) in polymer light-emitting diodes (PLEDs). The work function of the material (5.18 eV) was similar to that (5.20 eV) of a conventional conducting polymer dispersion, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrene sulfonate (PSS). When we fabricated PLEDs by using this material, the current–voltage–luminescence characteristics were very similar to those of the device using the PEDOT/PSS. When the material was blended with PSS, the luminous efficiency was further improved up to 11.9 cd/A. Since this kind of soluble type HIL has advantages over the conventional PEDOT/PSS dispersion in terms of the solution processibility and film quality, this soluble graft-type conducting polymer can be one of the promising candidates for a HIL in PLEDs.

Keywords: Light-emitting diodes; Hole injection layers; Conducting polymers

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1. Introduction

Over the past decade, polymer light-emitting diodes (PLEDs) have been attracting much attention due to the attractive applications such as large-size, flat or flexible panel displays which can be manufactured at low cost by solution process [1]. Achieving balanced electron–hole injection/transport is important to make efficient PLEDs. Indium-tin-oxide (ITO) and indium-zinc-oxide (IZO) have been used mostly as an anode in PLEDs since one of the electrodes in the devices is required to be transparent. However, the ITO and IZO surface deposited on glass is usually uneven with a large peak-to-trough value, which causes non-uniform electric field and thus accelerated device degradation [2,3]. Incorporating an additional conducting polymer layer such as polyaniline (PANI), polypyrrole, poly(3,4-ethylenedioxythiophene) (PEDOT), and a hyperbranched phthalocyanine on top of the ITO anode in PLEDs can improve the device efficiency and the lifetime by enhancing the hole injection from the ITO and planarizing the ITO surface [2–8]. Commercially available polymer materials for hole injection layers (HILs) are Baytron P series from H.C. Starck, GmbH which are based on PEDOT and polystyrene sufonate (PSS) in aqueous dispersion [2,3]. However, since PEDOT/PSS is dispersed in water with a large particle size (average: ca. 60 nm) [3], control of the particle size for the film quality can be another issue. The polymer dispersion would be difficult to be used for large-size panel displays as the aggregated particles can generate defects in the film. As a result, hole injection materials

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which are soluble in water or organic solvents are required but its performance should be at least comparable to the conventional PEDOT/PSS dispersion.

In this letter, we introduce a novel soluble (i.e. not a colloidal) and self-doped conducting polyaniline graft copolymer (PSS-*g*-PANI) for the HIL in PLED. This material is soluble in polar solvents such as dimethyl formamide as well as in water. Therefore, the film forming process can be done in an inert glove box which can prevent the water uptake from the film during the device fabrication process. Generally, PEDOT/PSS is not only precipitated from solution during storage, caused by aggregating particles slowly, but also difficult to be re-dispersed from the aggregated solids because PEDOT/PSS is not soluble but dispersible in water [3]. However, this graft-type conducting polymer can be maintained to be a clear solution during storage in solution [9]. On the other hand, PEDOT/PSS can be dissociated into PSS salt and PEDOT at higher pH (>pH 9), but in the case of the graft-type conducting polymer, the polymeric acid dopant, PSS is structurally stable in wide range of pH because the acid dopant is covalently bonded [9,10]. In addition, there is an advantage that the work function and the conductivity of PSS-*g*-PANI can be tuned by control of amount of aniline in synthetic steps [10]. Since the work function (5.18 eV) of PSS-*g*-PANI film turned out to be similar to that (5.20 eV) of conventional PEDOT/PSS (1:6 by wt.), the current–voltage–luminescence (*I*–*V*–*L*) characteristics of the device using PSS-*g*-PANI were similar to the device using the conventional PEDOT/PSS. In addition, we demonstrates a better luminous efficiency in the device using a reformulated conducting polymer composition, in which the PSS-*g*-PANI was molecularly mixed with PSS, compared with that in the device using the conventional PEDOT/PSS.

2. Experimental

2.1. Material synthesis

Fig. 1 shows the chemical structure of the conducting polymer, PSS-*g*-PANI which is completely soluble and self-doped conducting polyaniline graft copolymer [9]. The material was simply synthesized through the oxidative polymerization of aniline with oxidant and aqueous solution of random copolymer composed of stryenesulfonate and *p*-aminostyrene derivatives according to the literature [9]. In order to use the novel graft-type conducting polymer as a HIL for PLED, it is necessary to reduce its conductivity to avoid crosstalk between the pixels. Since the concentration of aniline unit in the conducting polymer is a crucial factor to determine the conductivity [10], we synthesized the conducting polymers whose conductivities were suitable for hole injection materials (conductivity $< 1 \times 10^{-3}$ S/cm). As shown in Scheme 1, we basically followed the reaction procedure according to Refs. [9,10] and specially controlled the concentration of aniline in oxidative polymerization step. First, in order to synthesize PSS-*g*-PANI, to solution of *p*-aminostyrene (1.19 g, 10.0 mmol) dissolved in dioxane (50 mL), di-*tert*-butyloxy dicarbonate, $(BOC)_2O$ (2.72 g, 12.5 mmol) and triethylamine (1.26 g, 12.5 mmol) were added and then the reaction mixture was stirred at 100 °C. After 15 h, 150 mL of petroleum ether and 150 mL of deionized (DI) water were added in sequence. The organic phase was separated, washed three times with

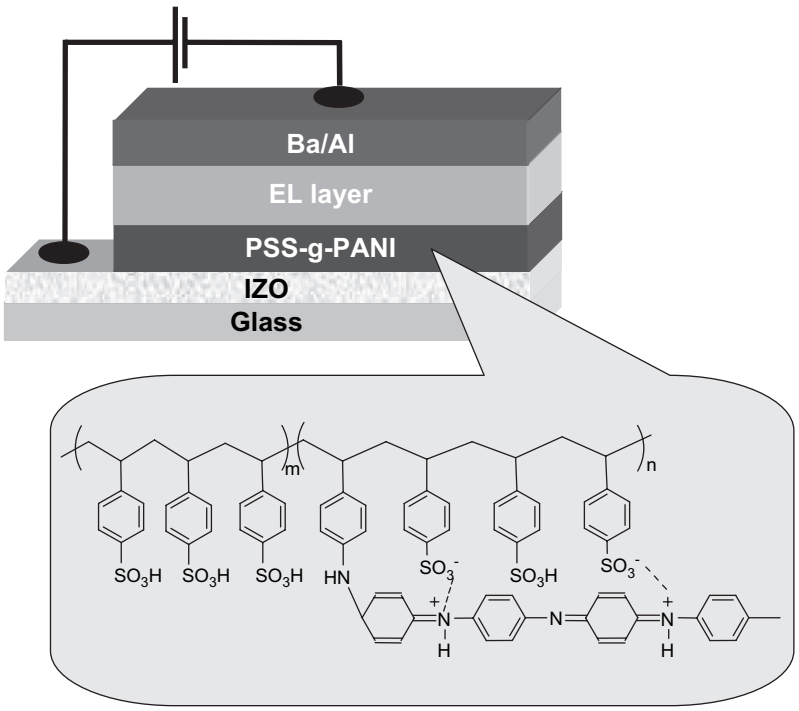
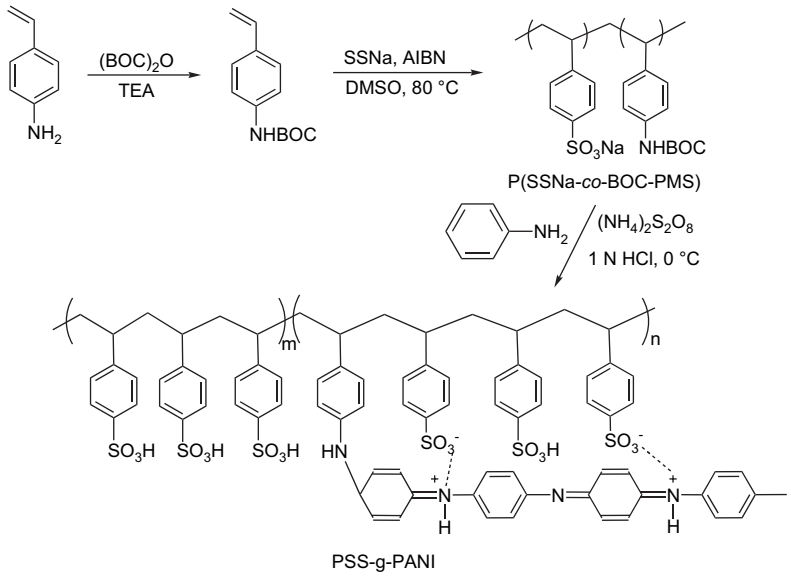


Fig. 1. Chemical structure of PSS-*g*-PANI and the device structure of green emitting diodes using PSS-*g*-PANI as a hole injection layer.



Scheme 1. Synthetic scheme for graft-type conducting polymer, PSS-*g*-PANI. $(BOC)_2O$ = di-*tert*-butyl dicarbonate, BOC = *tert*-butyloxy carbonyl, SSNa = sodium styrenesulfonate, P(SSNa-*co*-BOC-PMS) = poly(sodium styrenesulfonate-*co*-BOC-*p*-aminostyrene).

DI water and concentrated under reduced pressure. The crude product, BOC-aminostyrene, was recrystallized from ether to yield a white solid in 50%. Second, P(SSNa-*co*-BOC-PMS) was synthesized by copolymerizing SSNa and BOC-aminostyrene by using 2,2′-azo-bis(isobutyronitrile) (AIBN) as an radical initiator. SSNa (5 g, 24.2 mmol) and BOC-aminostyrene (106 mg, 0.484 mmol) were dissolved in 60 mL of DMSO and then the reaction temperature increased to 80 °C. AIBN was drop-wise added for 5 h by using syringe pump under N_2 atmosphere. After polymerizing for 36 h, the product was precipitated with acetone, filtered, washed several times with acetone and dried in vacuum oven at 60 °C for 48 h. Finally, for graft copolymerization of aniline onto P(SSA-*co*-aminostyrene), to 30 mL of HCl aqueous solution (1 M), 0.8 g of P(SSNa-*co*-BOC-PMS) was added. After stirring for 0.5 h, 0.1 g (1.07 mmol) of aniline was added to a solution of the reaction mixture. The reaction mixture was stirred vigorously until the reaction solution cleared, and then after cooling at 0 °C, 20 mL of ammonium persulfate (244 mg, 1.07 mmol) dissolved in 1 N HCl aqueous solution was drop-wise added by syringe pump. After stirring for 6 h, a dark green solution was filtered and purified by dialysis membrane (molecular weight cutoff 3500). The resulting solution was precipitated in acetone and dried in vacuum oven at 60 °C. The product, PSS-*g*-PANI, was obtained in 80% yield and the molar ratio of PSS to PANI is 1:0.15.

2.2. Film surface characterization

Surface morphologies and roughness were characterized by using an atomic force microscopy (Veeco Instruments, Model Dimension 3100) equipped with a carbon nanotube tip. Work functions of the HIL films were measured at an atmospheric pressure using an ultraviolet photoelectron spectrometer for usage in air (Surface Analyzer, Model AC-2, Riken-Keiki Co., Japan). The electrical conductivities of the conducting graft copolymer were measured at room temperature by the four-point probe technique using an electrometer.

2.3. Device fabrication and characterization

A commercially available PEDOT/PSS dispersion (Baytron P VP AI4083) was purchased from H.C. Starck, GmbH. Two different HIL films (PSS-*g*-PANI and PEDOT/PSS) in water were deposited by spin-coating method on top of indium-zinc-oxide (IZO: work function 5.1 eV) in air to achieve 60 nm thickness. Then, the films were baked on the hotplate in N_2 glove box at 200 °C for 10 min. A green emitting polyfluorene derivative (LUMATION 1300 series Green Polymer, Dow Chemical Company, $M_n = 190{,}000$, $M_w = 350{,}000$, HOMO: −5.55 eV, lowest unoccupied molecular orbital: −3.05 eV) dissolved in toluene was spin-coated on the HILs to obtain 70 nm thickness, which was subsequently baked at 130 °C for 60 min. The 5 nm Ba and 150 nm Al were sequentially deposited on the emitting layer under vacuum below 5×10^{-7} Torr. The PLED devices were encapsulated with a glass lid by using a UV curable epoxy resin. The *I*–*V*–*L* characteristics were obtained with a Keithley 238 source-measure unit and a Photo Research PR650 spectrophotometer.

3. Results and discussion

First of all, we characterized the conductivity and the surface roughness of the HIL films. The conductivity of this self-doped conducting polymer is ca. 1.0×10^{-4} S/cm. The root-mean-square roughness of the spin-coated PSS-*g*-PANI by atomic force microscopy was 0.628 nm for 10×10 μm^2 scan area, which is lower than that of PEDOT/PSS film

(1.350 nm). Therefore, our material can be more appropriate to be utilized as a HIL in top-emission OLED displays which requires high uniformity of the films to precisely control the emission colors as well as in bottom-emission OLED displays. We also observed the work function values of spin-coated PSS-*g*-PANI and PEDOT/PSS films by ultraviolet photoelectron spectroscopy in air, which is an analyzer for detecting low energy electrons emitted from a solid surface in air. The threshold energy of photoelectron emission is the work function or the ionization potential of the solid. Fig. 2 shows that the work function of PSS-*g*-PANI was 5.18 eV which is very similar to that of PEDOT/PSS (5.20 eV).

Fig. 3 shows the *I*–*V*–*L* characteristics of the devices using PEDOT/PSS and PSS-*g*-PANI HILs. The *I*–*V*–*L* characteristics of the two devices are very similar, which could be attributed to the similar work function values of the two HIL materials. If we take a closer look at the figures, while the current density of the device using PSS-*g*-PANI was slightly higher than that of the device using PEDOT/PSS, the luminance of the device using PSS-*g*-PANI was slightly lower than that of the device using PEDOT/PSS. Therefore, the luminous efficiency of the device using PSS-*g*-PANI was a little lowered (5.0 cd/A) compared with that of the device using PEDOT/PSS (7.3 cd/A) as Fig. 4 shows. We attributed this to the non-optimized molar ratio of PSS chains to PANI chains in the polymers (currently 1:0.15). We could achieve much higher luminous efficiency after optimizing the material structure (the ratio of PSS to PANI) during the synthesis. Since the conducting unit in the polymer can be a quenching center for excitons [11], the concentration of the aniline conducting unit should be minimized as far as the hole injection capability is maintained. In addition, PSS possesses an electron blocking characteristic which causes an increased field for hole injection due to the buildup of electrons at the interface [12]. On the other hand, the increase of the PSS content should result in reduced conductivity of the HIL. Therefore, the PSS in the conducting polymer should have the optimum molar concentration for HIL. In a previous literature, Higgins et al. reported that the PANI/PSS HIL in poly(2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) devices increased a luminous efficiency a little in spite of the increased operating voltages [5]. However, the PANI/PSS HIL in latter-type methyl-poly(*p*-phenylene) devices performed very

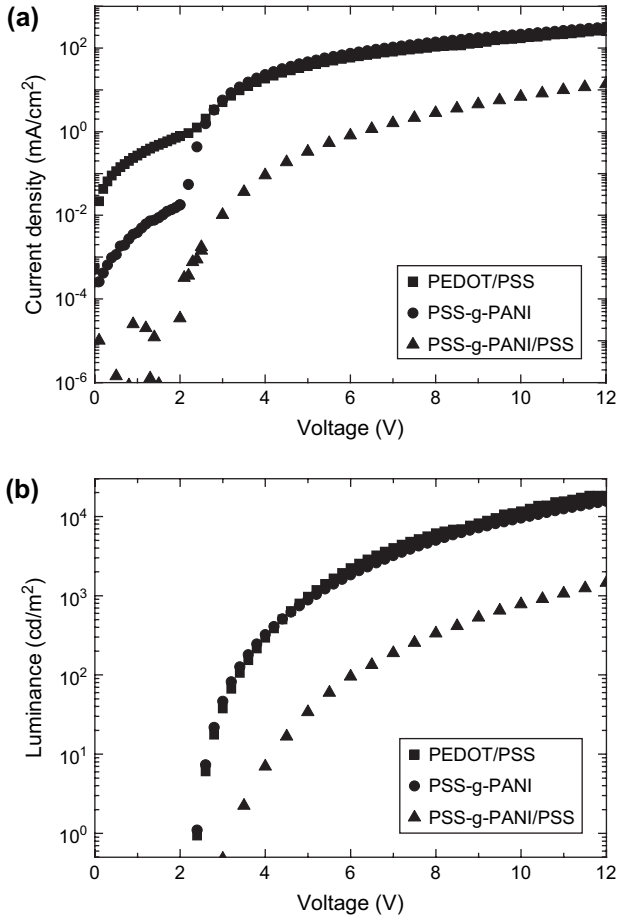


Fig. 3. Current–voltage–luminescence characteristics of green emitting polymer light-emitting diodes devices using PEDOT/PSS, PSS-*g*-PANI, and a reformulated PSS-*g*-PANI/PSS as the hole injection layers. (a) Current density versus voltage characteristics and (b) luminance versus voltage characteristics.

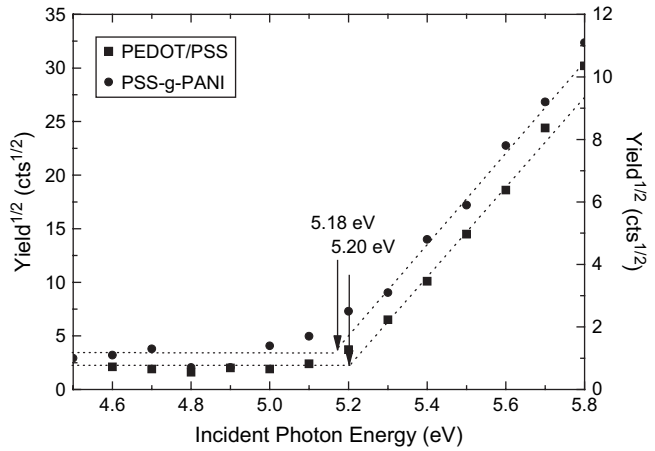


Fig. 2. Work functions of PSS-*g*-PANI and PEDOT/PSS films by ultraviolet photoelectron spectrometer (AC-2).

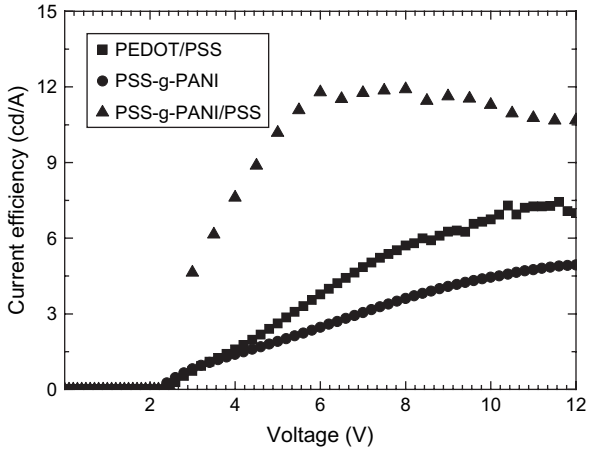


Fig. 4. The luminous efficiency of the devices using PEDOT/PSS, PSS-*g*-PANI, and a reformulated PSS-*g*-PANI/PSS as the hole injection layers.

poorly. Therefore, they concluded that the PANI/PSS HIL will not be suitable for devices based on polyfluorene derivatives having a wider bandgap than MEH-PPV. However, the polyfluorene device using our PSS-*g*-PANI HIL showed very similar current density and luminance characteristics with those using the PEDOT/PSS layer. They also studied the effect of the PSS content in the composition on the device performance. The optimum ratio of PANI to PSS was 1:5 by weight while the conventional PEDOT/PSS (Baytron P VP AI4083) has 1:6 weight ratio [5]. Since the ratio of PSS to PANI in PSS-*g*-PANI (1:0.15) is a little higher than the ratio of PSS to PEDOT (6:1), the conductivity (ca. 1.0×10^{-4} S/cm) is a little lower than that of PEDOT/PSS (ca. 6.0×10^{-4} S/cm) but the current density is almost the same. It is notable that the leakage current of the device using the PSS-*g*-PANI layer below 2 V becomes lower by two orders of magnitude than that using the PEDOT/PSS layer even without increasing the operating voltage. This will be an advantage of the PSS-*g*-PANI layer over the PEDOT/PSS layer. Recently, Mantovani et al. reported that spin-coated PEDOT/PSS material was found to consist of horizontal layers of flattened PEDOT-rich particles that are separated by quasi-continuous PSS lamella [13]. This film morphology leads to a strong anisotropic conduction that the lateral conduction along the substrate is much higher than the vertical conduction. Therefore, when the PEDOT/PSS film is used as a HIL, the crosstalk between the pixels can occur. In this case, the PEDOT/PSS film should be patterned or the composition should be diluted with extra PSS. However, since PSS-*g*-PANI is completely soluble, we can avoid this kind of strong anisotropic conduction problem.

Although we have not tried to find the optimum ratio of aniline to PSS in PSS-*g*-PANI, we show that the luminous efficiency of the devices could be further improved by molecularly mixing PSS-*g*-PANI with PSS, which is much simpler way than by synthesizing the conducting polymer with the same ratio of PSS to PANI in order to check the effect of the molar ratio of PSS to PANI in the polymer indirectly. We reformulated by addition of PSS into the PSS-*g*-PANI by 10:1 weight ratio in water solution. As shown in Fig. 4, the luminous efficiency was further increased up to 11.9 cd/A by using the reformulated PSS-*g*-PANI/PSS composition. The extra PSS tends to be rich at the film surface [14] so that it can help the electrons to be blocked at the HIL/emitting layer interface. Therefore, electrons and holes are more balanced for radiative recombination in the device. However, as Fig. 3a shows, the current density of the device using the reformulated composition is largely reduced, indicating that the electrons are greatly blocked by insulating PSS surface layer or the hole conduction through the PSS-*g*-PANI/PSS film layer is also reduced. Higgins et al. also reported that as the PSS content increases in the PANI/PSS composition, the current density tends to decrease at given voltages [5]. Currently, we are now investigating systematically on the effect of the extra polymeric acid (i.e. PSS) on the device performance and on alternatives of the graft-type conducting polymers such as polypyrroles, polythiophenes, etc.

4. Conclusion

We demonstrate that a novel soluble and self-doped conducting PANI graft copolymer can be effectively used for HIL in PLEDs. The film based on this graft-type conducting polymer showed similar work function level (5.18 eV) to that (5.20 eV) of conventional PEDOT/PSS. As a result, the *I*–*V*–*L* characteristics of the device using PSS-*g*-PANI were very similar to those of the devices using PEDOT/PSS. We showed that the composition can be further optimized by reformulating PSS-*g*-PANI by the addition of PSS into PSS-*g*-PANI. When we fabricated PLED by using this reformulated material, the device efficiency was much improved compared with that of the device using PEDOT/PSS. Since this kind of soluble type HIL has advantages over the conventional PEDOT/PSS dispersion in terms of the solution processibility and film quality for top-emission mobile displays as well as large-size panel displays, this graft-type conducting polymer can be one of the promising candidates for a HIL in organic/polymer light-emitting diodes.

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, et al. Nature 1990;347:539.
[2] Elschner A, Bruder F, Heuer HW, Jonas F, Karbach A, Kirchmeyer S, et al. Synth Met 2000;111–112:139.
[3] The information is available in the H.C. Starck website, http://www.hcstarck.com/.
[4] Yang Y, Westerweele E, Zhang C, Smith P, Heeger AJ. J Appl Phys 1995;77:694.
[5] Higgins RWT, Zaidi NA, Monkman AP. Adv Funct Mater 2001;11:407.
[6] Carter SA, Angelopoulos M, Karg S, Brock PJ, Scott JC. Appl Phys Lett 1997;70:2067.
[7] Gao J, Heeger AJ, Lee JY, Kim CY. Synth Met 1996;82:221.
[8] (a) Lee TW, Kwon O, Kim MG, Park SH, Chung J, Kim SY, et al. Appl Phys Lett 2005;87:231106;
(b) Lee TW, Chung Y, Kwon O, Park JJ. Adv Funct Mater 2007;17:390;
(c) Park J, Kwon Y, Lee TW. Macromol Rapid Commun 2007;28:1366;
(d) Lee TW, Kwon Y, Park JJ, Pu L, Hayakawa T, Kakimoto MA. Macromol Rapid Commun 2007;28:1657.
[9] Bae WJ, Kim KH, Park YH, Jo WH. Chem Commun 2003;22:2768.
[10] Bae WJ. PhD thesis, Seoul National University, 2005.
[11] Kim JS, Friend RH, Grizzi I, Burroughes JH. Appl Phys Lett 2005;87:023506.
[12] Murata K, Cina S, Greenhan NC. Appl Phys Lett 2001;79:1193.
[13] Nardes AM, Kemerink M, Janssen RJA, Bastiaansen JAM, Kiggen NMM, Langeveld BMW, et al. Adv Mater 2007;19:1196.
[14] Hwang J, Amy F, Kahn A. Org Electron 2006;7:387.