Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photovoltaic Properties of Dye-Sensitized Solar Cells Using Glycerol-Modified PEDOT:PSS

Jin-Kook Lee [a], Sung-il Jang [a], Bo-Hwa Jung [a], Hyong-Ju Choi [a], Su-Bin Lee [a], Sung-Hae Park [a] & Mi-Ra Kim [a]

[a] Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

Version of record first published: 26 May 2010

To cite this article: Jin-Kook Lee, Sung-il Jang, Bo-Hwa Jung, Hyong-Ju Choi, Su-Bin Lee, Sung-Hae Park & Mi-Ra Kim (2009): Photovoltaic Properties of Dye-Sensitized Solar Cells Using Glycerol-Modified PEDOT:PSS, Molecular Crystals and Liquid Crystals, 505:1, 175/[413]-183/[421]

To link to this article: http://dx.doi.org/10.1080/15421400902946194

Mol. Cryst. Liq. Cryst., Vol. 505, pp. 175/[413]–183/[421], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902946194

Photovoltaic Properties of Dye-Sensitized Solar Cells Using Glycerol-Modified PEDOT:PSS

Jin-Kook Lee, Sung-il Jang, Bo-Hwa Jung, Hyong-Ju Choi, Su-Bin Lee, Sung-Hae Park, and Mi-Ra Kim
Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

In this study, we fabricated Dye-Sensitized Solar Cell (DSSC) device using poly(3,4-ethylenedioxythiophene):poly(styrenesulphonic acid) (PEDOT:PSS) or glycerol-modified PEDOT:PSS (G-PEDOT:PSS) as hole conducting materials.

In SnO_2:F/TiO_2/Dye/PEDOT:PSS (or G-PEDOT:PSS)/Pt device system, in order to increase the ionic conductivity, the addition of ionic liquid into PEDOT:PSS solution resulted in the increase of power conversion efficiency of devices. We investigated photovoltaic characteristics of three type devices of SnO_2:F/TiO_2/Dye/G-PEDOT:PSS/Pt system according to glycerol concentration in PEDOT:PSS. The SnO_2:F/TiO_2/Dye/G-PEDOT:PSS/Pt device with 6 wt% glycerol in PEDOT:PSS showed the best result on 2.62% of the power conversion efficiency. The open-circuit voltage (V_{oc}) of this device was 0.82 V, the short-circuit current density (J_{sc}) was 5.48 mA/cm^2, and fill factor (FF) was 0.59.

Keywords: dye-sensitized solar cells (DSSCs); glycerol-modified PEDOT:PSS; hole conducting material; photovoltaic properties; poly(3,4-ethylenedioxythiophene): poly (styrene sulphonic acid) (PEDOT:PSS)

1. INTRODUCTION

Recently, DSSC has been widely investigated as a new type of solar cell because of its low production cost, simple structure, easy production, and higher power conversion efficiency (10%) [1,2]. However, the presence of traditional liquid electrolytes in these cells has some

This work was supported by the Ministry of Information & Communications, Korea, under the Information Technology Research Center (ITRC) Support Program.

Address correspondence to Mi-Ra Kim, Department of Polymer Science and Engineering, Pusan National University, Jangjeon-dong, Guemjeong-gu, Busan 609-735, South Korea. E-mail: mrkim2@pusan.ac.kr

problems such as a less long-term stability and a need for hermetic sealing. To overcome these problems, several studies of solid-state charge transport materials (i.e., electron or hole conducting materials) and quasi-solid-state electrolyte with ionic conducting polymer were attempted [3,4].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the best-known conducting polymers, and has attracted considerable commercial and scientific interest owing to its excellent conducting and electro-optical properties. PEDOT is an insoluble polymer that exhibits several desirable properties in its oxidized state: high conductivity (ca. 550 Scm^{-1}); good thin-film transparency; and high stability [5–8]. The low solubility of pure PEDOT may be circumvented by using a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS) as a charge-balancing dopant during polymerization in water to yield a PEDOT:PSS composite [9]. PEDOT:PSS also has high transparency in visible range, high conductivity and remarkable stability at room temperature [9], so that PEDOT:PSS could work as a stable hole transport material [5] and utilize in a wide range of electrochemical devices such as polymer light-emitting diodes (PLED) [10], organic solar cells [11], and ink jet printing technology [12].

Donal D. C. Bradley has shown that the resistivity of PEDOT:PSS can be decreased without any loss in its optical characteristics through addition a small amount of a polyalcohol such as glycerol [13].

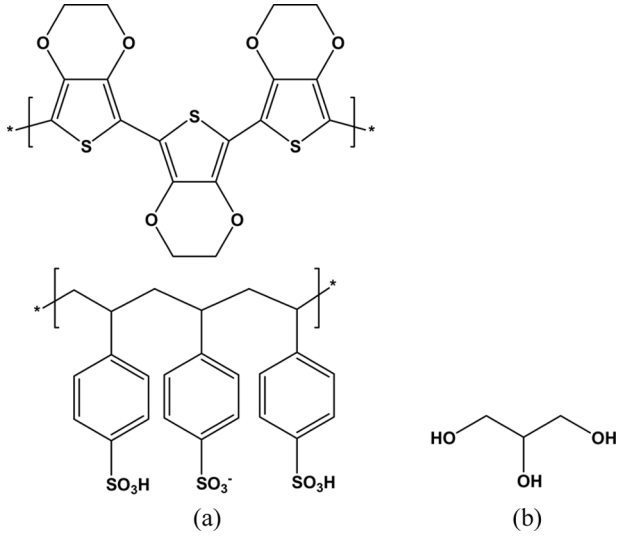

FIGURE 1 The chemical structures of (a) PEDOT:PSS and (b) Glycerol.

This conductivity gain and optic transparency maintenance are potential characteristics of glycerol-modified PEDOT:PSS (G-PEDOT:PSS) to improve organic devices efficiency [10,14]. Figure 1 shows the chemical structures of PEDOT:PSS and glycerol.

In this study, we report the fabrications and photovoltaic properties of SnO_2:F/TiO_2/Dye/PEDOT:PSS or G-PEDOT:PSS/Pt devices using PEDOT:PSS or G-PEDOT:PSS as hole conducting materials. In addition, the influence on the surface morphology of PEDOT:PSS and G-PEDOT:PSS layers on devices by the addition of the glycerol was investigated.

2. EXPERIMENTAL

2.1. Materials

TiO_2 paste (Ti-Nanoxide HT/SP), cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) dye (N3 dye), F-doped SnO_2 glass (FTO glass, 15 Ω/square), Pt paste (Pt catalyst T/SP) were purchased from Solaronix Co. The PEDOT:PSS and glycerol were purchased from H. C. Starck (Germany) and Aldrich Co, respectively.

2.2. Fabrication of DSSC Devices

The dye-sensitized solar cells (DSSCs) were constructed by a dye-adsorbed nanoporous titanium oxide (TiO_2) electrode as a working electrode, a Pt-counter electrode, and an electrolyte filled with between two electrodes. The working electrode was prepared as follows. The TiO_2 paste with 9 nm particle size was placed on an FTO glass by doctor blade method, followed by sintering at 120°C for about 30 min and at 450°C for about 30 min in air to give a TiO_2 electrode with an effective area of 0.25 cm^2. The nanoporous TiO_2 electrode was dipped in N3 dye solution that dye was dissolved in a concentration of 10 mg of N3 dye per 50 ml of absolute ethanol solution at room temperature over night. The dye adsorbed TiO_2 electrode was dipped in electrolyte solution at room temperature for 24 hours. The electrolytes are contained of 72 mg of tetrabutylammonium iodide (TBAI), 80 mg of 1-ethyl-3-methyl imidazolium iodide (EMImI) as an ionic liquid, 80 ml of PEDOT:PSS, or G-PEDOT:PSS as hole conducting materials, and 0.32 ml of ethylene carbonate (EC)/0.08 ml of propylene carbonate (PC) (EC: PC = 4:1 v/v). In order to fabricate an all-solid state DSSC and improve the problem by the evaporation of I_2, I_2 was not used. After that, the electrolyte was casted onto dye-adsorbed nonporous TiO_2 electrode and was dried at about

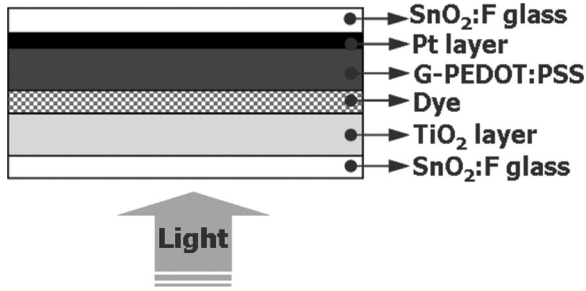

FIGURE 2 The structure of the SnO_2:F/TiO_2/Dye/G-EDOT:PSS/Pt device.

100°C for 2 hours. The counter electrode was also prepared by the similar method to TiO_2 electrode. Pt paste was placed on an FTO glass by doctor blade method, followed by sintering to at 450°C for 30 min with 5°C/min of heating rate.

In assembling of devices, the working electrode and the counting electrode were clamped together and the intervening space between two electrodes was filled the polymer electrolyte. The structure of SnO_2:F/TiO_2/Dye/Electrolyte/Pt device was shown in Figure 2.

2.3. Measurements

The surface morphology of the electrolyte layers was measured in air with a Scanning Probe Microscope (SPM, NITECH Models SPA-400).

Measurement of the I-V characteristics of devices was carried out using a Solar Simulator (300 W simulator, models 81150) under simulated solar light with ARC Lamp power supply (AM 1.5, 100 mW/cm^2).

3. RESULTS AND DISCUSSION

We have made of solid-state-DSSC devices, SnO_2:F/TiO_2/Dye/Electrolyte/Pt devices using PEDOT:PSS or G-PEDOT:PSS as hole conducting materials. The thicknesses of the devices were about 10 μm of nanoporous TiO_2 layer and 3 μm of electrolyte layer.

The ionic liquid addition to the cell with PEDOT also improved significantly the dark current property of the cells, which result in the increase of open-circuit voltages (V_{oc}) ($0.75 \rightarrow 0.81$) and fill factor (FF) ($0.34 \rightarrow 0.49$) in photocurrent characteristics [5]. In addition, Lu *et al*. reported that the addition of ionic liquids was improved the physical properties of conducting polymers [15]. The ionic liquid could form the electrical double layer at SnO_2:F/PEDOT:PSS or TiO_2/PEDOT:PSS interface, preventing the unfavorable contact of the

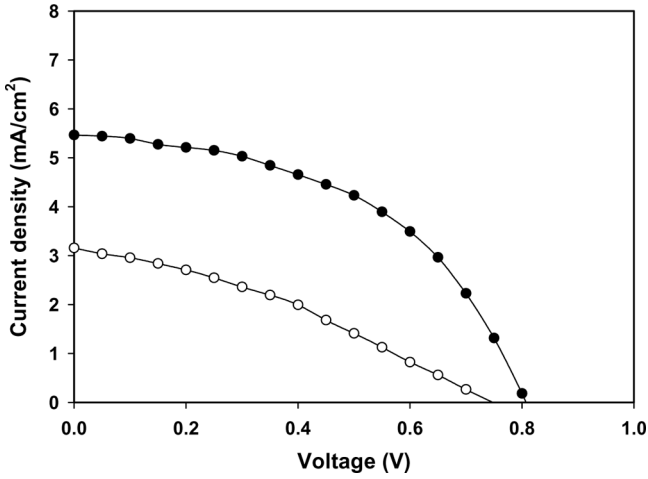

FIGURE 3 The photovoltaic characteristics of SnO_2:F/TiO_2/Dye/PEDOT:PSS/Pt devices under AM 1.5; ● = PEDOT:PSS without EMImI, ○ = PEDOT:PSS with EMImI; light intensity: 100 mW/cm^2; active area: 0.25 cm^2.

PEDOT:PSS at these interfaces which cause electron recombination in the cells. As shown in Figure 3, the power conversion efficiency of SnO_2:F/TiO_2/Dye/PEDOT:PSS/Pt devices with ionic liquid was higher than that of device without ionic liquid. Consequently, the power conversion efficiency of the device by the introduction of ionic liquid such as EMImI was improved.

The influence on the photovoltaic effects of SnO_2:F/TiO_2/Dye/G-PEDOT:PSS/Pt devices using PEDOT:PSS by the addition of the glycerol is shown in Figure 4 and photovoltaic characteristics of devices are summarized in Table 1.

In Table 1, the results of V_{oc} were obtained the high values of $0.78 \sim 0.82$ V on SnO_2:F/TiO_2/Dye/PEDOT:PSS or G-PEDOT:PSS/Pt devices system regardless of glycerol concentration [16].

The power conversion efficiencies of devices were changed by the introduced glycerol into the PEDOT:PSS for different ratios of 1 wt%, 6 wt%, and 10 wt%. These results were caused by changes in the conductivity and the morphology of PEDOT:PSS layers. The conductivities of G-PEDOT:PSS layers increase with the concentration of added glycerol [13]. Significant improvements in conductivity are observed even for low concentration of added glycerol. These increased conductivities of the films in the presence of the glycerol are believed to arise from the rearrangement of the PEDOT:PSS morphology. Also, by the drying process at 100°C, the solvent such as water in

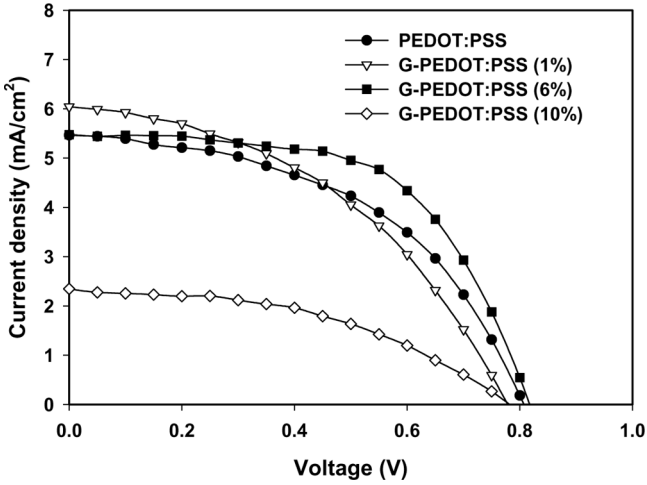

FIGURE 4 The photovoltaic characteristics of SnO_2:F/TiO_2/Dye/PEDOT:PSS (or G-PEDOT:PSS)/Pt devices (a) in the dark (b) under AM 1.5; light density: 100 mW/cm^2; active area: 0.25 cm^2.

PEDOT:PSS or G-PEDOT:PSS solution can be evaporated sufficiently. The morphological and physical changes during G-PEDOT:PSS film formation by this drying process are considered more likely to account for the improved conductivity. These changes cause that the overall connectivity between PEDOT grains in G-PEDOT:PSS films was improved. This should create better pathways for charge transport perpendicular to the film. In general, J_{sc} values of DSSC device was influenced by the ionic conductivity of polymer electrolyte. Figure 5

TABLE 1 The Photovoltaic Characteristics of SnO_2:F/TiO_2/Dye/PEDOT:PSS (or G-PEDOT:PSS)/Pt Devices Using PEDOT:PSS or G-PEDOT:PSS as Hole Conducting Materials Under AM 1.5 Illumination. 1-Ethyl-3-metyl Imidazolium Iodide (EMImI) as an Ionic Liquid was Added into Electrolytes of All Devices

	V_{oc}[a] (V)	J_{sc}[b](mA/cm^2)	FF[c]	Efficiency (%)
PEDOT:PSS	0.81	5.46	0.49	2.14
G-PEDOT:PSS (1 wt%)	0.78	6.04	0.43	2.03
G-PEDOT:PSS (6 wt%)	0.82	5.48	0.59	2.62
G-PEDOT:PSS (10 wt%)	0.79	2.35	0.45	0.82

[a]V_{oc}(V): Open circuit voltage.
[b]J_{sc}(mA/cm^2): Short circuit current density.
[c]FF: Fill factor.

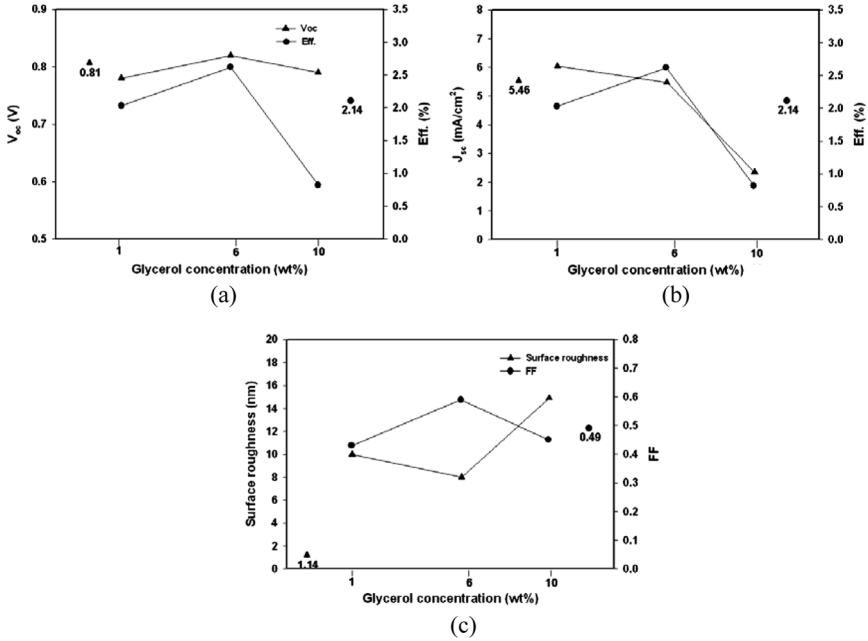

FIGURE 5 The dependence of photovoltaic performances of SnO_2:F/TiO_2/Dye/PEDOT:PSS (or G-PEDOT:PSS)/Pt devices on the different glycerol concentration (wt%); (a) V_{oc} and Eff.; (b) J_{sc} and Eff.; (c) Surface roughness and FF. Also shown for comparison is the characteristics of the devices using the PEDOT:PSS layer as separating point.

shows the dependence of device properties on glycerol concentration. It is found that J_{sc} decreases with the increase of glycerol concentration.

In order to investigate the relationships between the morphology of PEDOT:PSS or G-PEDOT:PSS films on the device and the power conversion efficiency of the device, we measured the surface morphology of PEDOT:PSS and G-PEDOT:PSS films by Scanning Probe Microscope (SPM).

The changes in the morphology of PEDOT:PSS layer and G-PEDOT:PSS layers with different glycerol concentration are illustrated in the AFM surface images at Figure 6. The surface roughness of PEDOT:PSS layers was remarkably decreased by the addition of the ionic liquid such as EMImI. Also, the surface roughness of layers varied with the glycerol concentration. As Figure 5 shows, this improvement of surface morphology on G-PEDOT:PSS layers results in the increase of fill factor. The surface morphology of G-PEDOT:PSS layers was remarkably increased by the addition of 6 wt% glycerol.

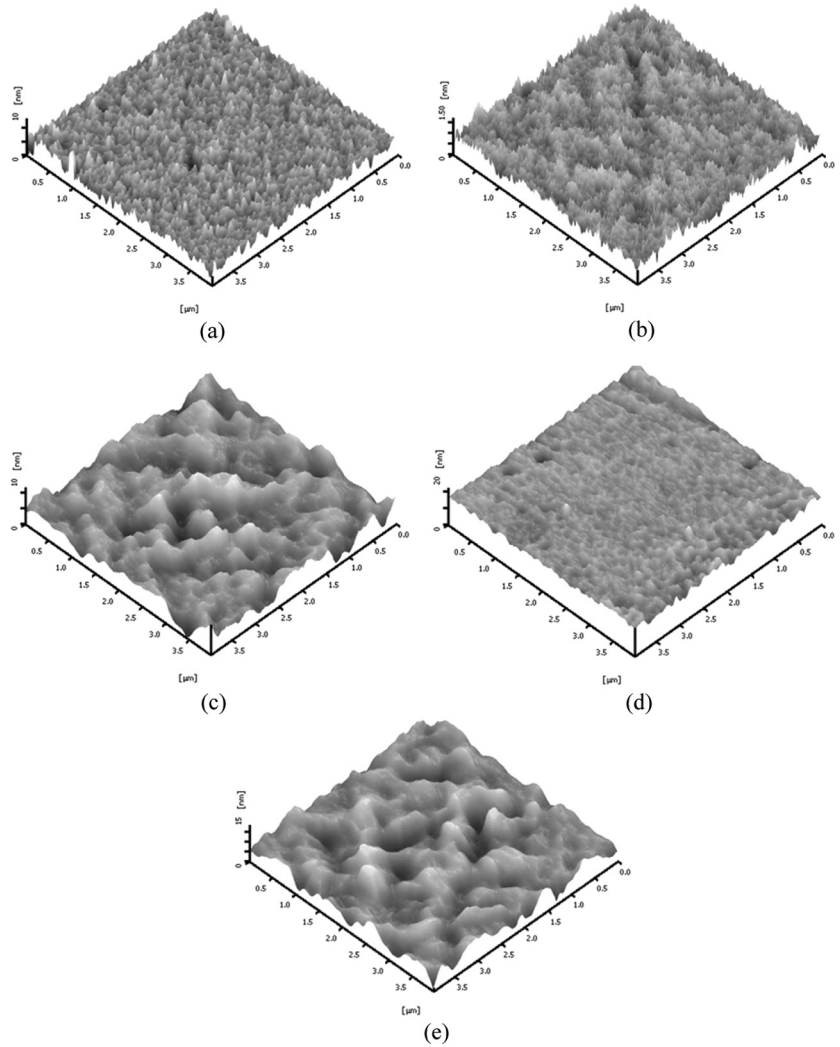

FIGURE 6 The AFM images of (a) PEDOT:PSS layer without EMImI; (b) PEDOT:PSS layer containing EMImI; (c) G-PEDOT:PSS layer (1 wt%) containing EMImI; (d) G-PEDOT:PSS layer (6 wt%) containing EMImI; (e) G-PEDOT:PSS layer (10 wt%) containing EMImI; image sizes are $4\,\mu m \times 4\,\mu m$.

Considering both the J_{sc} value from conductivity and layer uniformity, 6 wt% of glycerol concentration is considered optimum. As a result, the DSSC device using G-PEDOT:PSS (6 wt%) exhibited the

highest value of power conversion efficiency, η of 2.62% among all the devices.

4. CONCLUSIONS

We have successfully prepared the solid-state-DSSC devices using PEDOT:PSS or G-PEDOT:PSS as hole conducting materials. The EMImI addition to the cell with PEDOT:PSS results in the increase of power conversion efficiency of DSSC devices. Moreover, AFM results showed that the morphology of layers was improved by the introduction of EMImI.

The photocurrent of the device decreased with the increase of glycerol concentrations, although the open-circuit voltages of the device little changed. Considering both the J_{sc} value from conductivity and FF from surface roughness of layer, glycerol concentration of 6 wt% is considered optimum on SnO_2:F/TiO_2/Dye/G-PEDOT:PSS/Pt device.

REFERENCES

[1] O'regen, B. & Gratzel, M. (1991). *Nature*, *353*, 737.
[2] Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Muller, E., Liska, P., Valchopoulos, N., & Gratzel, M. (1993). *J. Am. Chem. Soc.*, *115*, 6382.
[3] Tennakone, K., Fermando, C. A. N., Dewasurendra, M. J., & Photochem, J. (1997). *Photobio. A: Chem*, *38*, 75.
[4] Komiya, R., Han, L., Yamanaka, R., Islam, A., Mitate, T., & Photochem, J. (2004). *Photobio. A: Chem*, *164*, 123.
[5] Jonas, F. & Schrader, L. (1991). *Synth. Mat.*, *831*, 41.
[6] Heywang, G. & Jonas, F. (1992). *Adv. Mater.*, *4*, 116.
[7] Winter, I., Reece, C., Hormes, J., Heywang, G., & Jonas, F. (1995). *Chem. Phys.*, *194*, 207.
[8] Groenendaal, L., Jonas, F., Freitag, D., Pielartik, H., & Reynolds, J. R. (2000). *Adv. Mater.*, *12*, 481.
[9] Jonas, F., Krafft, W., & Muys, B. (1995). *Macromol. Symp.*, *100*, 169.
[10] de Kok, M. M., Buechel, M., Vulto, S. I. E., van de Weijer, P., Meulenkamp, E. A., de winter, S. H. P. M., Mank, A. J. G., Vorstenbosch, H. J. M., Weijtens, C. H. I., & van Elsbergen, V. (2004). *Phys. Stat. Sol.*, (a) *201*, 1342.
[11] Gang, Li, Vishal, S., Jinsong, H., Yan, Y., Moriarty, T., Emery, K., & Yang, Y. (2005). *Nature Materials Adv. Online. Pub.*, *10*, 1038.
[12] Natori, A. Y., Canestraro, C. D., Roman, L. S., & Ceschin, A. M. (2005). *Mat. Sci. Eng.*, B *122*, 231.
[13] Huang, J., Miller, P. F., Wilson, Jo S., Andrew, J., de Mello, J. C., de Mello, Donal., & Bradley, D. C. (2005). *Adv. Funct. Mater.*, *15*, 290.
[14] Kim, J. K., Jung, J. H., Lee, D. E., & Joo, J. (2002). *Synth. Met.*, *126*, 311.
[15] Lu, W., Fadeev, A. G., Qi, B., Smela, E., Mattes, B. R., Ding, J., Spinks, G. M., Mazurkiewicz, J., Zhou, D., Wallace, G. G., Macfarlane, D. R., Forsyth, S. A., & Forsyth, M. (2002). *Science*, *297*, 983.
[16] Mozer, A. J., Wada, Y., Jiang, K. J., Masaki, N., Yanagida, S., & Mori, S. N. (2006). *Appl. Phys. Lett.*, *89*, 043509.