DOI: 10.1002/masy.201051040

Poly(3,4-ethylenedioxythiophen)/Poly(4-styrenesulfonate): Thin Films and Microfibers

Hu Yan, Hidenori Okuzaki**

Summary: This Feature Article describes our recent researches on processing poly(3,4-ethylenedioxythiophene /poly(4-styrenesulfonate) (PEDOT/PSS) colloidal dispersion into thin films which exhibit high conductivity and high transparency, and into microfibers which exhibit high conductivity and high mechanical strength. The state-of-the-art thin films and microfibers are expected to utilize to sophisticated touch screens and wearable electronic devices as organic transparent electrodes and woven electric circuits, respectively.

Keywords: colloids; conducting polymers; fibers; thin films

Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with a suitable arylsulfonate compound attracted R&D researchers' great attention since their excellent conductivity and thermal stability in applications for solid electrolyte capacitors.[1–3] The solid electrolyte capacitors fabricated by using the doped PEDOT as a cathode showed excellent high-frequency properties and thermal stability.[3]

Since colloidal dispersion was realized by using a water-soluble polyelectrolyte poly(4-styrenesulfonate) (PSS),[4] poly(3,4-ethylenedioxythiophene)/ poly(4-styrenesulfonate) (PEDOT/PSS) has been, furthermore, extensively studied from viewpoints of academic and technologic aspects.[5–7] The PEDOT/PSS has been a widely available conductive polymer since the colloidal dispersion of the PEDOT/PSS in water enables easily provide films on various substrates by simple means such as solution casting and spin-coating techniques.[8,9] The colloidal dispersion also allows to easily process the PEDOT/PSS into microfibers by a wet-spinning technique.

In this short Feature Article, we concentrated on our recent researches where nanometer-scaled thin film and microfibers were prepared by wet-process such as spin-coating and wet-spinning which are benefitted from the colloidal dispersion of the PEDOT/PSS.

PEDOT/PSS Thin Films

Primary Particle-Monolayer[10]

Although there have been many reports on synthesis and electronic properties as well as application of PEDOT/PSS few researches have been reported from viewpoint of colloid science. Recently we investigated PEDOT/PSS dispersion (BAYTRON PH500, denote PH) by dynamic light scattering (DLS) measurements. As a result, the PH dispersion contained PEDOT/PSSS primary particles with an average diameter of 16 nm, as shown in Fig. 1. The PEDOT/PSS thin films were prepared by spin-coating on smooth silicon wafers under a rotating speed of 3000 rpm. Figure 2 shows cross-sectional scanning transmission electron microscopic (STEM) image of the thin film. The PEDOT/PSS layer is sandwiched by top protecting layer and bottom silicon substrate in the STEM image. The thickness of the PEDOT-PSS film was 16 nm. The agreement of the thickness with the primary particle

---

Laboratory of Organic Robotics, Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-4-37 Takeda, Kofu 400-8511, Japan
Fax: (+81) 55 220 8706;
E-mail: okuzaki@yamanashi.ac.jp;
yanhu@yamanashi.ac.jp

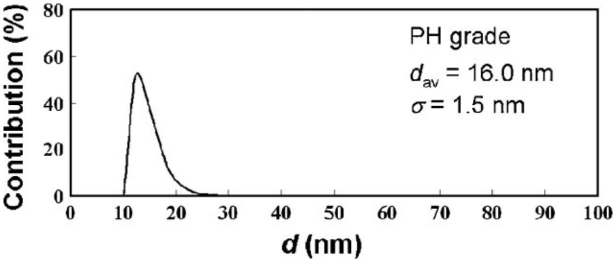

Figure 1.
Particle size distribution of PH grade PEDOT/PSS solutions measured by DLS. Reprinted from Ref. [10], Copyright 2009, with permission by Elsevier.

diameter suggests that the PEDOT/PSS thin film is made by a ‘‘primary particle-monolayer’’. Is it true?

To answer the question we performed C_{60}-sputtering X-ray photoelectron spectroscopic (XPS) measurement over entire cross-section of the PEDOT/PSS film, as shown in Fig. 3. The XPS spectra showed well-signed peaks at around 169 and 165 eV due to S_{2p} of PSS and PEDOT moieties, respectively.[11] The second peak due to PEDOT, significantly lower before the sputtering, drastically increased with increasing in the sputtering time and finally decreased. The PEDOT/PSS ratio calculated based on the XPS spectra was plotted in inset of Fig. 3.

A structure of PEDOT grain surrounded by PSS shell was proposed by Greczynski et al.[11] Hwang et al. also pointed out the existence of top PSS layer with a thickness of ca. 35 Å in the PEDOT/PSS film based on their argon-sputtering XPS measurement.[12] If the PEDOT-core/PSS-shell particles well packed in a monolayer in the PEDOT/PSS thin film the top and bottom layers of the film should be predominantly rich in PSS, therefore, PEDOT/PSS ratio should drastically increase from top surface to inner domain on the cross-section of the thin film, and then keep in constant cross inner domain, and finally drastically decreases to bottom surface attached on the silicon substrate. The correlation between diameter of primary particle and thickness of the thin film revealed that the PEDOT/PSS thin films consist of ‘‘monolayer’’ of the PEDOT/PSS

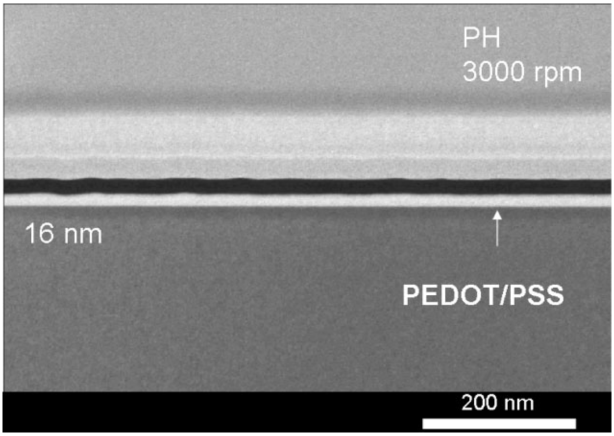

Figure 2.
STEM image of spin-coated PEDOT/PSS film with rotating rate of 3000 rpm using PH grade PEDOT/PSS solution. Reprinted from Ref. [10], Copyright 2009, with permission by Elsevier.

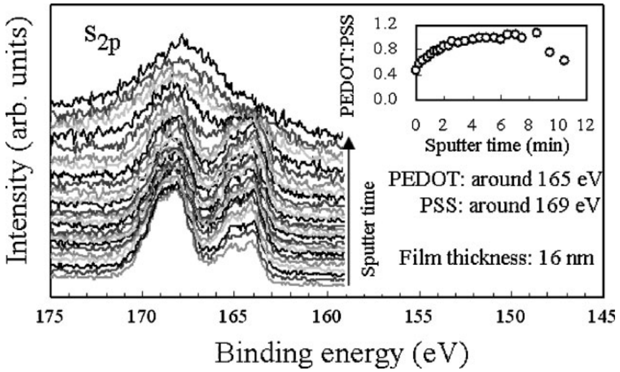

Figure 3.

C_{60}-sputtering XPS spectra of the spin-coated PEDOT/PSS film with 3000 rpm using PH grade solution. Inset: The changes of PEDOT:PSS ratio with the sputtering time, calculated based on the XPS data. Reprinted from Ref. [10], Copyright 2009, with permission by Elsevier.

primary nanoparticles, which was also reasonably supported the agreement of the thickness with the primary particle diameter, and by the results of the C_{60}-sputtering XPS measurements.

Aggregation by Solvent-Treatment[13]

It is well known that addition of certain organic solvent such as dimethylsulfoxide (DMSO) and ethylene glycol (EG) during preparation of the PEDOT/PSS films is able to significantly improve conductivity of the films. The enhancement mechanism, however, is still argued. To obtain further insights about the mechanism we investigated the solvent effect in terms of film thickness of the primary particle-monolayer. The PEDOT/PSS thin films were prepared by spin-coating on smooth silicon or SiO_2/Si substrates with roughness of ca. 0.1 nm, under a rotating rate of 3000 rpm. The thickness of the PEDOT/PSS films increased with adding EG in the PH solution regardless the substrate. As mentioned, the 16 nm-thick PEDOT/PSS thin film consists of the primary particle-monolayer. Therefore, the increase of the film thickness by the addition of the EG may be induced by i) the increase of the primary particle diameter, or ii) the aggregation of two or three primary particles (cluster). In the clusters the size of the primary particle should decrease by removing the excess PSS layer.

PPS molecules are suggested to be washed away by the organic solvent from the surface region of the PEDOT/PSS film, resulting in higher PEDOT:PSS ratio on the surface of the film.[14] It can be considered that the diameters of the primary particles would decrease by the wash-effect, resulting in thinner film if it is the monolayer of the primary particles. The film thickness observed in the present work, however, increased by the addition of the EG. Therefore, it is considerable that the PEDOT/PSS thin films spin-coated from PH EG3% may consist of aggregates of primary particles with decreased diameters by the wash-effect.

To elucidate the effect of the EG on PEDOT:PSS ratio we performed XPS measurement using the PEDOT/PSS thin films spin-coated from PH and PH EG3% solutions, respectively. The XPS spectra showed well-signed peaks at around 169 and 165 eV due to S_{2p} of PSS and PEDOT moieties, respectively. The peak due to PEDOT moiety significantly increased with the addition of the EG, indicating increasing in the PEDOT:PSS ratio of the thin film. On the other hand, the O 1s spectra showed peaks at around 533 and 531 eV, assigned to PEDOT and PSS moieties, respectively. The PEDOT:PSS ratios of the thin films prepared using PH and PH EG3% solutions were calculated by the peak area of S_{2p} spectra to be 0.55 and 0.62, respectively.

It is easily considerable that the roughness of the film surface would increase after the EG addition since the suggested clusters contain several primary particles. We have investigated surface roughness (R_a) by the AFM measurements. The surface of the film prepared using PH EG3% solution was rougher than that of PH. The roughness R_a, estimated from the images, was 0.66 and 0.72 nm for the PH and PH EG3% films, respectively.

We carried out conductive-probe microscopic measurements on the thin films by AFM with a contact mode, as shown in Fig. 4. The AFM current images clearly showed that the PEDOT-rich particles randomly and loosely packed on the silicon surfaces. The higher conductive spots in the PH EG3% film was much larger than the PH one either in size or in number, indicating that the grains enlarged and PEDOT:PSS ratio increased within the individual grains. The result coincided with the fact that thickness and roughness of the film increased by the EG addition.

The above results suggested that primary nanoparticles decrease in size but aggregate by removing excess PSS after the EG addition, which is consistent with that PEDOT:PSS ratio, roughness, number of highly conductive grains and thickness of the PEDOT/PSS thin film coincidently increase with the EG addition. It should be noted that the sheet resistance was as high as 10 MΩ/sq. even for the PH EG3% film probably because loose packing of the clusters or particles although the conductivity within the individual grains (vertical conductivity estimated by the AFM current image) were much increased. The high sheet resistance or the poor parallel conductivity, however, would hinder practical application of the PEDOT/PSS thin films with an excellent transparency to electronic devices such touch screens and *e*-papers.

Highly Conductive and Highly Transparent Thin Films[15]

Colloidal particles with narrow size distribution would compactly pack each other, which could provide highly conductive PEDOT/PSS thin films coupled with a removal of the excess PSS-rich layer. Therefore, we investigated centrifuge effect on the colloidal dispersion in terms of the film conductivity.

The centrifuge effect on conductivity and surface roughness were investigated in detail. The electrical conductivity significantly increased with increasing in the rotating rate of centrifuge. It is considerable that the PEDOT/PSS colloidal particles with a narrower size distribution more compactly pack each other in the thin film, resulting in higher conductivity. On the other hand, the surface roughness decreased in increasing in the rotating speed. It is also indicated that the particle size distribution of the packed PEDOT/PSS particles is narrower, resulting in more smooth surface of the thin film.

We have carefully optimized the EG concentration in terms of conductivity and transmittance of visible-light. The conductivity increased with increasing in the EG concentration while the transmittance was unchanged. The highest estimated value of the conductivity, 443 S/cm was obtained at the EG concentration of 7%, coupled with high value of the transmittance of 89%. Noting that the film prepared under the same condition but only without the centrifuge showed only moderately high conductivity, 263 S/cm, which clearly reveals the enhancement of conductivity by the centrifuge which would result in narrower size distribution of the PEDOT/PSS colloidal particles.

PEDOT/PSS Microfibers

Preparation of Highly Conductive Microfibers by Wet-Spinning[16,17]

PEDOT/PSS microfibers were fabricated by a wet-spinning technique. Typically, about 1 ml of a PEDOT/PSS dispersion solution was poured in to a glass cylinder and extruded into coagulation bath containing aceteone through a single-hole spinneret with inner diameter of 70 μm. The resulting micrfibers were wound on a

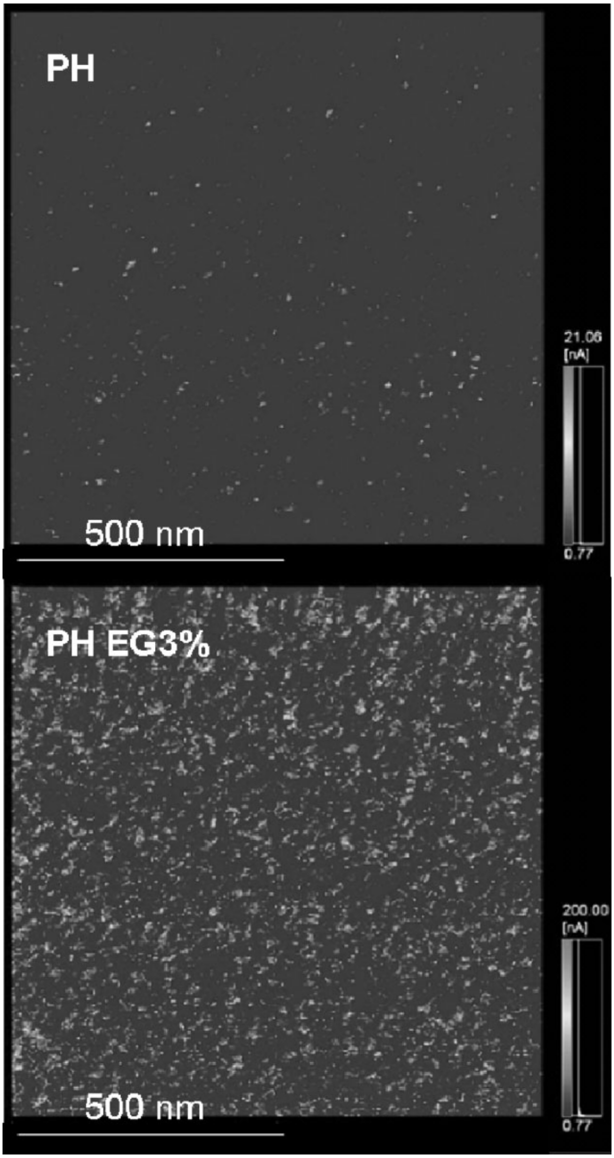

Figure 4.
AFM current images of PEDOT/PSS thin films spin-coated on Si substrates at 3000rpm using PH (top) and PH EG3% (bottom) solutions. Reprinted from Ref. [13], Copyright 2009, with permission by Elsevier.(Under application of permission).

spool and dried in vacuum overnight. Diameter of the PEDOT/PSS microfibers were depended on the spinning conditions. In an optimized condition we fabricated the PEDOT/PSS microfibers with diameter of *ca.* 5 μm which was measured by scanning electron microscopic (SEM) observations, as shown in Fig. 5.

The PEDOT/PSS microfibers thus-fabricated were used for dipping-treatment of EG in order to improve the conductivity of the microfibers. Surprisingly but interestingly it was found that the conductivity of the PEDOT/PSS microfibers were significantly improved by the EG-dipping treatment. Typically the conductivity increased

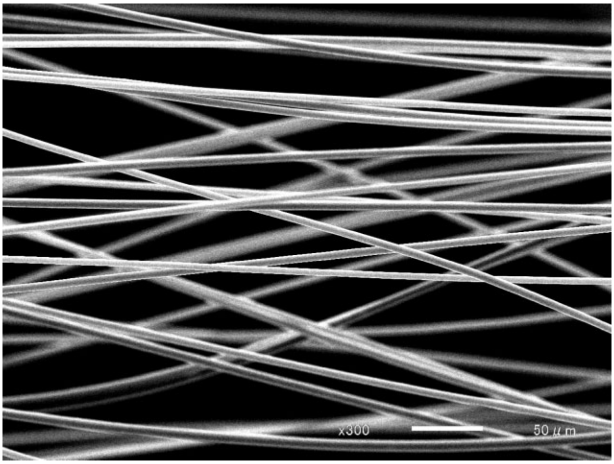

Figure 5.
SEM image of typical PEDOT/PSS microfibers. Reprinted from Ref. [17], Copyright 2009, with permission by Elsevier.

from 73 to 475 Scm^{-1} for that from PH dispersion only in the dipping time of 3 min, as shown in Fig. 6. It is noteworthy that the value of conductivity is highest among the previously reported PEDOT/PSS fiber or films to date, to the best of our knowledge. The conductivity was kept in constant even when the dipping time was extended to 30 min.

Mechanical properties of the fibers are crucially important for the applications of such kind of microfibers. Furthermore change of the mechanical properties by the dipping treatment may provide useful insights to take account for the improvement of the conductivity. We measured Young's modulus and tensile strength of the microfibers before and after the dipping treatment of EG in detail. The Young's modulus and tensile strength of the dipping-treated PEDOT/PSS microfiber were 3.7 GPa and 125 MPa, respectively, while the Young's modulus and tensile strength of untreated one were 2.5 GPa and 98 MPa, respectively.

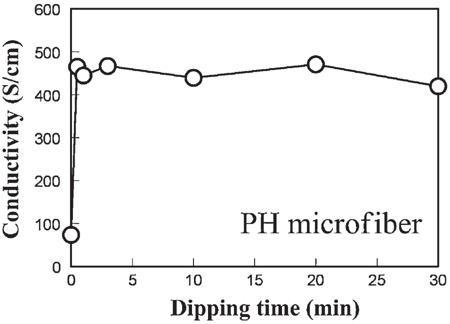

Figure 6.
Changes in conductivity of PEDOT/PSS microfiber spun from PH grade PEDOT/PSS solution by dip-treatment in EG. Prior to the measurement, the microfiber was dried at 160 °C in a vacuum for 1 h to remove the EG completely. Reprinted from Ref. [17], Copyright 2009, with permission by Elsevier.

The XRD patterns of PEDOT/PSS microfibers before and after dipping treatment of EG were measured. The XRD patterns of the microfibers before the dipping treatment showed halo, indicating that the microfibers are amorphous or low crystalline degree. The XRD patterns of the microfibers after the dipping treatment, however, showed obvious Debye-Scherrer-rings, clearly indicating increase of crystalline degree in the microfibers after the EG-dipping. It is considerable that PEDOT molecules in amorphous state stacked into crystalline state during the dipping and drying processes based on the Debye-Scherrer-rings assigned to (020) plane of an orthorhombic unit cell.[18] It is noteworthy that the obvious Debye-Scherrer-rings is first observations for the PEDOT/PSS fibers or films.

The PEDOT/PSS microfibers showed semiconducting characteristics in the temperature dependence of electrical conductivity. According to a nearest-neighbor hopping model, activation energies (E_a) were calculated to be 12 meV for the microfibers spun from PH dispersion. Surprisingly the activation energies of the microfibers significantly decreased to be 2.1 meV after the dipping treatment of EG. The results revealed that the electronic carriers easily conduct from one PEDOT domain to another due to better contacts among the domains after the EG-treating.

FET Channel Lengths Fabricated by Using the Microfiber as a Shadow Mask [19-23]

Organic field-effect transistors (FETs) are considered to be used in flexible flat displays as power source. Short channel length of the organic FET would provide large drain current. Conventionally such short channel length was patterned by using quite expensive shadow masks. Recently we reported facile fabrication of micrometer-scaled channel patterns of pentacene FETs by utilizing the wet-spun PEDOT/PSS microfibers with diameter of ca. 5 μm. The typical fabrication procedures are as follows: About 1 mL of a PEDOT/PSS dispersion solution was poured in to a glass cylinder and extruded into coagulation bath containing acetone through a single-hole spinneret with inner diameter of 70 μm. The resulting microfiber was carefully loaded on graph paper and dried in vacuum at 160 °C for 1 h before using as channel masks. A heavily doped n-type silicon wafer with a SiO_2 thin layer (350 nm) was washed in pure water and acetone, and UV-ozoning treatment was carried out in order to remove organic contaminants. Then, self-assembled mololayer (SAM) of octadecyltrichlorosilane (OTS) was prepared on the UV-ozoning treated substrate by immersing method. Subsequently pentacene was thermally deposited on the SAM-formed substrate. Finally gold was thermally deposited in vacuum on pentacene layer using the microfiber as the channel mask and the microfiber was easily eliminated by taking away to result in the channel pattern to finish the fabrication of the top-contacted FET. The pentacene FET with a top-contacted configuration showed a hole mobility of $0.13\,cm^2\,V^{-1}\,s^{-1}$ and on/off current ratio of 9.4×10^4. The device also showed large drain current of ca. 160 μA ($V_D = -50\,V$; $V_G = -50\,V$), reflecting shorter channel length (5 μm) of the devices.

We also prepared low-voltage pentacene FETs and air-stable pentacene/C_{60} ambipolar FETs by using the PEDOT/PSS microfiber-based channel patterning technique.

Conclusion

The centrifuge and solvent effects as well as the spin-coating technique provided highly conductive and highly transparent PEDOT/PSS thin films. The films are promising for wide applications to touch screens and e-papers. On the other hand, the highly conductive and mechanically strong microfibers can be fabricated by the wet-spinning technique coupled with solvent-treatment. The microfibers may become state-of-the-art materials for ‘‘woven circuits’’ of future wearable devices.

Acknowledgements: The authors gratefully acknowledge the financial support by Strategic Research Projects from University of Yamanashi, and the support from TOKYO ELECTRON LTD by founding Laboratory of Organic Robotics in University of Yamanashi in April, 2007.

[1] Y. Kudoh, K. Akami, Y. Matsuya, *Synth. Met.* **1999**, *102*, 973.
[2] S. Ghosh, O. Inganas, *Adv. Mater.* **1999**, *11*, 1214.
[3] F. Larmat, J. R. Reynolds, Y.-J. Qiu, *Synth. Met.* **1996**, *79*, 229.
[4] A. G. Bayer, Eur. Patent 440957, 1991.
[5] S. C. J. Meskers, J. K. J. van Duren, R. A. Janssen, *Adv. Funct. Mater.* **2003**, *13*, 805.

[6] A. L. Briseno, M. Roberts, M.-M. Ling, H.-S. Moon, E. J. Nemannick, Z. Bao, *J. Am. Chem. Soc.* **2006**, *128*, 3880.

[7] H. Yan, Y. Endo, Y. Hara, H. Okuzaki, *Chem. Lett.* **2007**, *36*, 986.

[8] A. M. Nardes, M. Kemerink, A. J. Janssen, J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, A. J. J. van Breemen, M. M. de Kok, *Adv. Mater.* **2007**, *19*, 1196.

[9] M. Kemerink, S. Timpanaro, M. M. de Kok, E. A. Meulenkamp, F. J. Touwslager, *J. Phys. Chem. B* **2004**, *108*, 18820.

[10] H. Yan, S. Arima, Y. Mori, T. Kagata, H. Sato, H. Okuzaki, *Thin Solid Films* **2009**, *517*, 3299–3303.

[11] G. Greczynski, Th. Kugler, W. R. Salaneck, *Thin Solid Film* **1999**, *354*, 129.

[12] J.-H. Hwang, F. Amy, A. Kahn, *Org. Electron.* **2006**, *7*, 387.

[13] H. Yan, H. Okuzaki, *Synth. Met.* **2009**, *159*, 2225.

[14] S. K. M. Jonsson, J. Birgerson, X. Crispin, G. Greczynski, W. Osikowicz, A. W. Denier van der Gon, W. R. Salaneck, M. Fahlman, *Synth. Met.* **2003**, *139*, 1.

[15] H. Yan, T. Jo, H. Okuzaki, *Polym. J.* **2009**, *41*, 1028.

[16] H. Okuzaki, M. Ishihara, *Macromol. Rapid Commun.* **2003**, *24*, 261.

[17] H. Okuzaki, Y. Harashina, H. Yan, *Eur. Polym. J.* **2009**, *45*, 256.

[18] K. E. Aasmundtveit, E. J. Samuelsen, L. A. A. Pettersson, O. Inganas, T. Johansson, R. Feidenhans'l, *Synth. Met.* **1999**, *101*, 561.

[19] H. Yan, T. Kagata, Y. Mori, Y. Harashina, Y. Hara, H. Okuzaki, *Chem. Lett.* **2008**, *37*, 44.

[20] H. Yan, T. Kagata, H. Okuzaki, *Synth. Met.* **2009**, *159*, 2229.

[21] H. Yan, T. Kagata, S. Arima, H. Sato, H. Okuzaki, *Phys. Stat. Soli. (a)* **2008**, *205*, 2970.

[22] H. Yan, T. Kagata, H. Okuzaki, *Appl. Phys. Lett.* **2009**, *94*, 23305.

[23] H. Yan, T. Uchida, T. Kagata, Y. Iriyama, H. Okuzaki, *Chem. Lett.* **2009**, *38*, 550.