

## Polymer Optoelectronic Devices with High-Conductivity Poly(3,4-Ethylenedioxythiophene) Anodes

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### ABSTRACT

The conductivity of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) film can be enhanced by more than two orders in magnitude by adding a compound with two or more polar groups, such as ethylene glycol (EG), *meso*-erythritol (IUPAC name: 1,2,3,4-tetrahydroxybutane), or 2-nitroethanol, into the PEDOT:PSS aqueous solution. The mechanism of the increase in conductivity for PEDOT:PSS has been studied using Raman spectroscopy and atomic force microscope (AFM). Here we propose that the change in conductivity is due to the conformational change of PEDOT chains in the film. In untreated PEDOT:PSS films, coil, linear, or expanded-coil conformations of the PEDOT chains may be present. In treated PEDOT:PSS films, the linear or expanded-coil conformations may become the dominant form for PEDOT chains. This conformational change results in the enhancement of charge-carrier mobility in the film and leads to enhanced conductivity. The high-conductivity PEDOT:PSS film is ideal as the electrode for polymer optoelectronic devices. In this article, we report on the fabrication of polymer light-emitting diodes (PLEDs) and photovoltaic cells (PVs) made using a

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highly conductive form of PEDOT:PSS as anode, and we demonstrate its performance relative to that of similar device using indium-tin oxide (ITO) as the anode.

*Key Words:* Conducting polymer; Poly(3,4-ethylenedioxythiophene); Optoelectronic devices.

## INTRODUCTION

Polymer electronics has been considered as a promising technology because of its light-weight, high flexibility, and solution-processible properties.<sup>[1]</sup> Electronic devices using polymer as the active material, such as polymer light-emitting diodes (PLEDs) and photovoltaic cells (PVs), exhibit promising performance. The goal is to achieve high performance and fully-plastic electronic devices. Major technical challenges come from the electrodes, since the solution-processible organic compounds usually have very low conductivity compared with inorganic counterparts. The high resistance of the organic electrodes lowers device performance, and the Joule heating generated by current flow through the organic electrodes decreases the lifetime of the device. For optoelectronic devices, at least one of the electrodes is required to be transparent. Although indium-tin oxide (ITO) is frequently used as the transparent electrode in flexible devices, its mechanical flexibility is limited, and cracks occur readily when the substrate is bent. This usually induces defects in the devices. Thus, it is required to develop organic-based electrodes with both high transparency and high conductivity for the plastic optoelectronics.

Poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) emerges as a promising material for electrodes in optoelectronic devices. It has many advantages over other conducting polymers, such as high transparency in the visible range, excellent thermal stability, and aqueous solution processibility.<sup>[2,3]</sup> Consequently, it has been widely used as a buffer layer for electrodes in organic electronics and a material for ink-jet printing.<sup>[4,5]</sup> However, PEDOT:PSS also suffers the low-conductivity problem. The commercially available PEDOT:PSS (Baytron P, Bayer Corporation) has a conductivity of less than 1 S/cm. This conductivity is lower than some other good conducting polymers by one to two orders in magnitude and lower than ITO by about three orders in magnitude. PLEDs or PVs using this low-conductivity PEDOT:PSS as the anode exhibit very low performance. Recently, it was observed that the conductivity of PEDOT:PSS film can be enhanced by more than an order in magnitude by adding polyalcohols (alcohols with more than two OH groups on the molecule) or high dielectric solvents, such as methyl sulfoxide (DMSO) and *N,N*-dimethylformamide into the PEDOT:PSS solution.<sup>[6–11]</sup> But the mechanism for this observed conductivity enhancement has been under debate. Inganäs et al. considered the high boiling polyalcohol as a plasticizer and under its aid the PEDOT:PSS chains reorient at high temperature to form a better connection between the conducting PEDOT chains.<sup>[6,7]</sup> Kim et al. proposed that the polar solvents with a high dielectric constant induce strong screening effects between positively charged PEDOT and negatively charged PSS dopant to reduce the Coulomb interaction between the counterions and the charge carrier.<sup>[9]</sup> Jönsson et al. argued that the reason for the conductivity enhancement was that PSS<sup>-</sup> chains are washed away from the surface region of the

PEDOT:PSS film during the film-forming process, so that a thin layer of high conductivity with high PEDOT concentration is formed on the surface of the film.<sup>[10]</sup> Organic light-emitting diodes and PVs using the modified PEDOT:PSS as the anode were fabricated but exhibited relatively poor performance.<sup>[8,11]</sup> In this article, we report a new mechanism for the conductivity enhancement of PEDOT:PSS film and the fabrication of PLEDs and PVs using the high-conductivity PEDOT:PSS film as the anode. Our devices exhibit high performance, close to those of the devices using ITO as the anode.

## EXPERIMENTAL

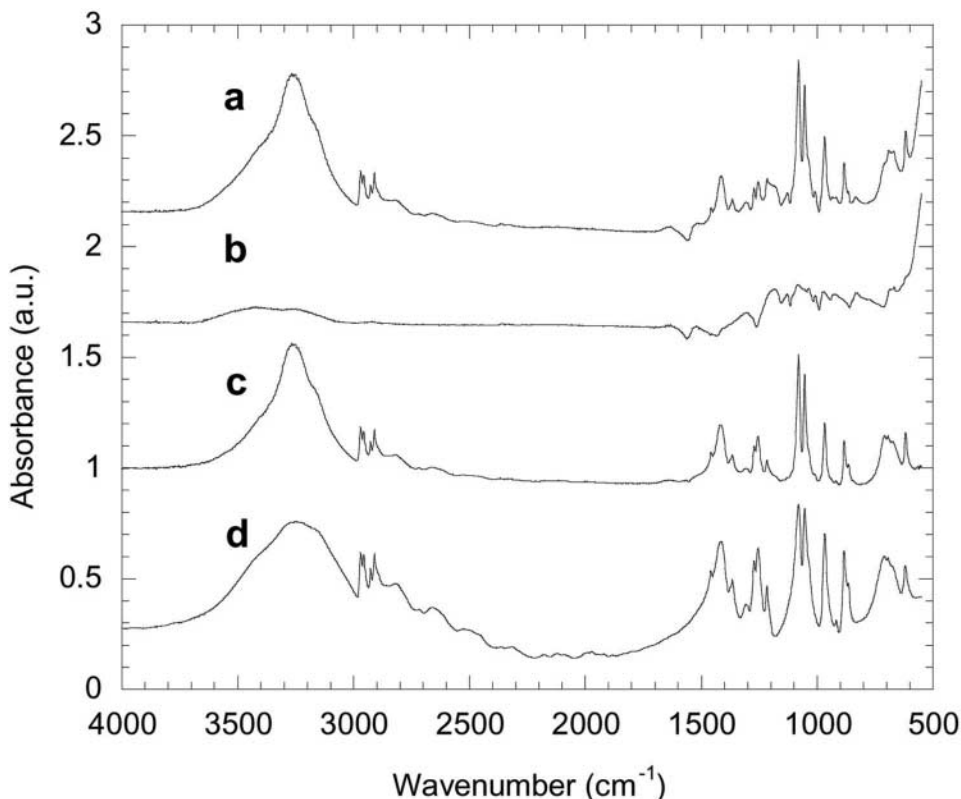
High-conductivity PEDOT:PSS films were formed on glass substrates by spin-coating the PEDOT:PSS (Baytron P, V4071) aqueous solution added with ethylene glycol (EG), *meso*-erythritol, DMSO, or 2-nitroethanol. The amount of liquid additive is 1:1 in volume to the PEDOT:PSS aqueous solution, and the amount of *meso*-erythritol is 300 mg in 5 mL PEDOT:PSS aqueous solution. The resistance of the PEDOT:PSS films was measured by the four-point probe technique. For Fourier transfer infrared spectrum (FTIR), PEDOT:PSS solutions with or without *meso*-erythritol were dropped cast on KBr pellets. The resulting films were baked at 150°C for 2 hr. After baking, the samples were grinded, and re-made to form new KBr pellets for transmission FTIR. The IR spectra were recorded by a Midas M2200 spectrometer. Raman spectra were taken on the polymer films with a Renishaw 1000 Raman system using 632.8 nm HeNe laser as the excitation in a back scattering configuration. The high-conductivity E-PEDOT:PSS films for Raman spectroscopy were obtained by spin-coating the *meso*-erythritol blended PEDOT:PSS aqueous solution and baked at 150°C for 30 min. Atomic force microscope (AFM) images were taken using a Digital Instruments NanoScope III equipped with an extender module box operating in tapping mode in ambient condition. The E-PEDOT:PSS films for AFM were obtained by spin-coating *meso*-erythritol blended PEDOT:PSS aqueous solution on glass substrate and then dried in vacuum for 4 hr. Some E-PEDOT:PSS films were subsequently baked at 150°C for 30 min for conductivity enhancement. PEDOT:PSS aqueous solution added with EG was spin-coated on glass substrates for the construction of PLEDs. Poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) solution in *p*-xylene was subsequently spin-coated. The cathode was formed by subsequent thermal deposition of Ca and Al on the MEH-PPV film. PEDOT:PSS aqueous solution added with *meso*-erythritol was spin-coated on the glass substrates to construct PVs. The polymer photovoltaic (PV) devices were fabricated by spin-coating MEH-PPV and methanofullerene (phenyl C<sub>61</sub>-butyric acid methyl ester) (PCBM) mixture solution (1:4 by weight) in 1,2-dichlorobenzene on the prepared anode. The active area of PLEDs and PVs is 0.12 cm<sup>2</sup>. The current–voltage (*I*–*V*) curves were obtained by a Keithley 2400 source-measure unit. The photocurrent for PVs was measured under illumination supplied by a Thermal Oriel 150W solar simulator (AM1.5G). All devices were fabricated and tested in nitrogen environment. The dipole moment of 3,4-ethylenedioxythiophene and thiophene was calculated using the HyperChem 7.1 program with PM3 semi-empirical method.

## RESULTS AND DISCUSSION

### Conductivity Enhancement of the PEDOT : PSS Film

The PEDOT : PSS film formed by spin-coating from aqueous solution (Baytron P V4071 from Bayer Corporation) has a conductivity of about 0.4 S/cm. This conductivity was enhanced by more than two orders in magnitude by adding ethylene glycol (EG), *meso*-erythritol (IUPAC name: 1,2,3,4-tetrahydroxybutane), DMSO, or 2-nitroethanol into the PEDOT:PSS aqueous solution. These results are similar to observations by other researchers.<sup>[6–11]</sup> Our further study indicates that the conductivity enhancement strongly depends on the chemical structure of the additive. When alcohol with only one OH group, such as methanol, ethanol, or heptanol was used, no conductivity enhancement was observed. Conductivity enhancement of the film was not observed as well when nitromethane or acetonitrile was added into the PEDOT : PSS aqueous solution. When EG was added into the PEDOT:PSS aqueous solution (EG–PEDOT : PSS represents the treated PEDOT : PSS), the conductivity of the film increases. The same conductivity enhancement was observed for the EG–PEDOT : PSS films dried in vacuum at room temperature or after baking at 100°C for 30 min. When *meso*-erythritol was added into the PEDOT : PSS aqueous solution (E-PEDOT : PSS represents this PEDOT : PSS) with the E-PEDOT : PSS film dried in vacuum at room temperature, no conductivity enhancement was observed. However, when the E-PEDOT : PSS film was baked at 150°C for 30 min, conductivity enhancement by more than two orders in magnitude was observed. The heating of the E-PEDOT : PSS film at 150°C may cause *meso*-erythritol, which has a melting point of 123°C and is a solid at room temperature, to liquefy. Conductivity enhancement by more than two orders was also observed by immersing a dried PEDOT : PSS film into EG.

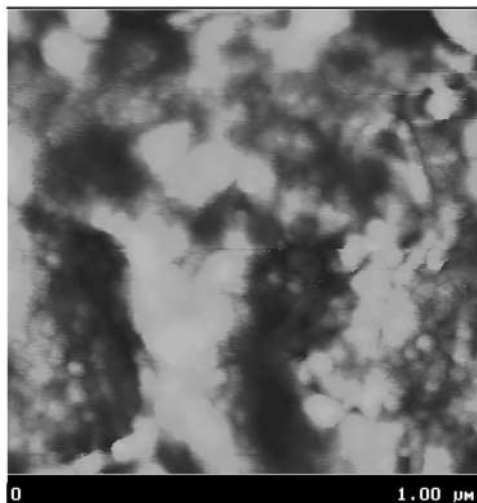
These results suggest that the mechanism for conductivity enhancement of the PEDOT : PSS film is different from those previously proposed. At least two reasons indicate that a wash-away of the PSS<sup>−</sup> chains from the film surface region proposed by Jönsson et al. should not be the mechanism for conductivity enhancement.<sup>[10]</sup> The first reason is increase in conductivity in the E-PEDOT : PSS film after heating at 150°C. Since PEDOT : PSS does not melt at this temperature and it is insoluble in liquid *meso*-erythritol, the ratio of PEDOT to PSS should stay the same before and after heating. The IR absorption spectra of the E-PEDOT : PSS film was recorded [Fig. 1(a)]. Compared with the untreated PEDOT : PSS film [Fig. 1(b)], several additional absorption peaks were observed. However, after subtracting the contribution from PEDOT : PSS, the resulting spectrum [Fig. 1(c)] has a well match with the spectrum of pure *meso*-erythritol [Fig. 1(d)]. This suggests that the IR absorption in Fig. 1(a) is simply the summation of the contributions from both PEDOT : PSS and *meso*-erythritol. A considerable amount of *meso*-erythritol still remains in the PEDOT : PSS films after heat treatment and no significant chemical reaction occurs during baking at 150°C. It is inferred that the remained polar groups is essential to the increase in conductivity of PEDOT : PSS. The conductivity enhancement by treating a dried PEDOT : PSS film with EG also supports that no wash-away of PSS<sup>−</sup> chains happens in the surface region, as the dried PEDOT : PSS polymer is insoluble in EG. Another reason is the observation of the independence of the conductivity enhancement on the film thickness. Our experiments suggest the conductivity enhancement mechanism proposed by Kim et al. is not true as well. Kim et al. proposed that the effect of the polar solvent is to induce a screening



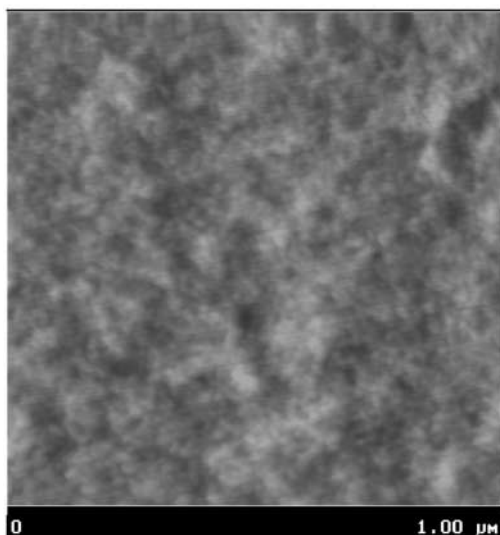
**Figure 1.** Transmission FTIR spectra of (a) PEDOT:PSS blended with *meso*-erythriol; (b) PEDOT:PSS; (c) PEDOT:PSS blended with *meso*-erythriol subtracted the contribution from PEDOT:PSS; (d) *meso*-erythriol. The similarity between spectra (c) and (d) suggests a considerable amount of *meso*-erythriol was left in the heat-treated PEDOT:PSS film.

effect between the counterions and the PEDOT chains.<sup>[9]</sup> However, our experiments found that the PEDOT:PSS film treated with EG ( $\epsilon = 37$ ,  $\epsilon$ : dielectric constant) has a conductivity higher than the PEDOT:PSS film treated with DMSO ( $\epsilon = 49$ ) by about 40%. Furthermore, no conductivity enhancement was observed when a compound of high dielectric constant, like nitromethane ( $\epsilon = 39$ ), methanol ( $\epsilon = 38$ ), or acetonitrile ( $\epsilon = 38$ ) was added into PEDOT:PSS aqueous solution. Our experiments also indicate that the additive does not play a role simply as a plasticizer proposed by Inganäs et al.<sup>[6,7]</sup> If the additive just simply acts as a plasticizer, other liquid additives like heptanol, which is liquid at room temperature and has a boiling point close to EG, should enhance the conductivity as well. However, no conductivity enhancement was observed. Moreover, our experiments indicate that the heating process does not play a role for the conductivity enhancement when liquid additive is added. We believe that an additive in the liquid state is important for conductivity enhancement, and may provide space for the reorientation of polymer chains. But the most important reason for the conductivity enhancement may be the interaction between the additive and the polymer chains.

To understand the mechanism for the conductivity enhancement, the E-PEDOT : PSS film morphology was studied by AFM before and after heating at 150°C. (Fig. 2) The film morphology changes after heating. It has a rough surface before heating and becomes quite smooth after heating. This morphologic change suggests reorientation of polymer chains after heating.



(a)

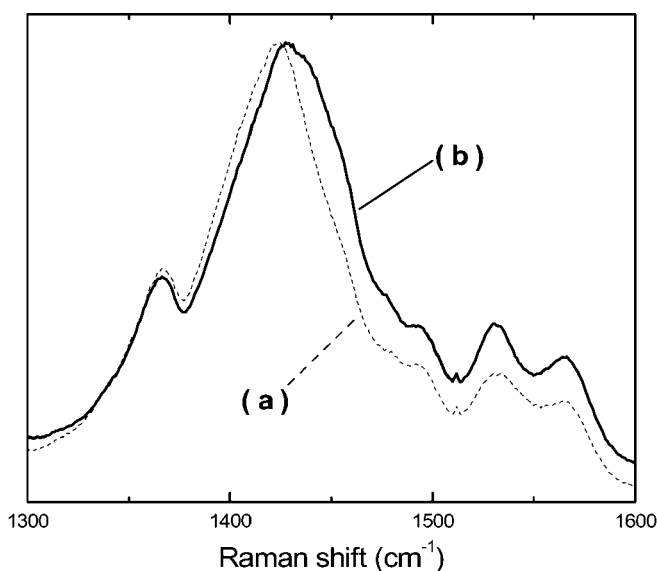


(b)

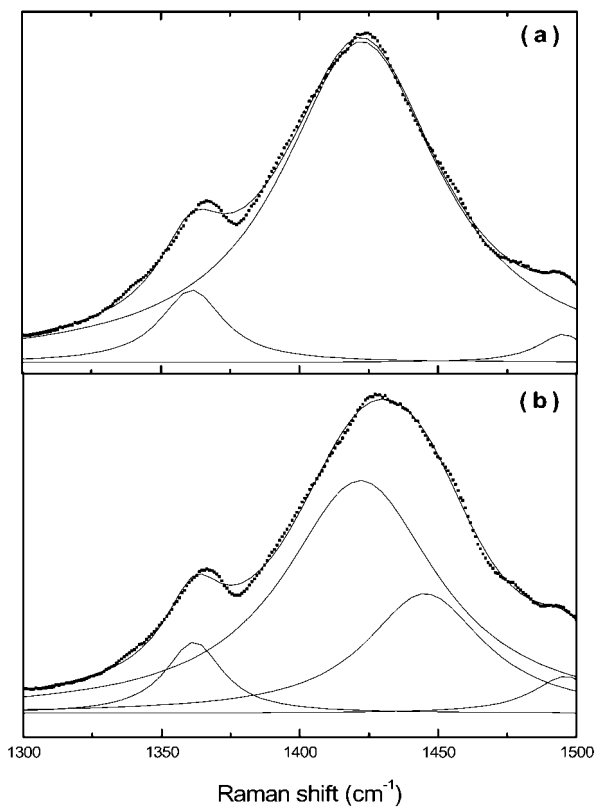
**Figure 2.** AFM pictures of PEDOT :PSS blended with *meso*-erythritol, (a) dried in vacuum at room temperature and (b) dried in vacuum, and subsequently baked at 150°C for 30 min.

To understand this change on a molecular level, the films were studied by Raman spectroscopy. Raman spectroscopy is a powerful tool to study conducting polymers.<sup>[12–15]</sup> The Raman spectra of the untreated PEDOT : PSS and the high-conductivity E-PEDOT : PSS films are shown in Fig. 3. The most obvious difference was observed on the strongest band between 1400 and 1500  $\text{cm}^{-1}$ . The high-conductivity E-PEDOT : PSS exhibited a narrower band at a lower position than the untreated PEDOT : PSS. A shoulder can be discerned for the untreated PEDOT : PSS. The band of the untreated PEDOT : PSS was deconvoluted into two vibrations at 1422 and 1445  $\text{cm}^{-1}$ , whereas the band for the high-conductivity E-PEDOT : PSS was fit well by only one vibration at 1422  $\text{cm}^{-1}$  (Fig. 4). The disappearance of the shoulder at 1445  $\text{cm}^{-1}$  indicates the effect of the additive on the chemical structure of the PEDOT chains in the PEDOT : PSS film.

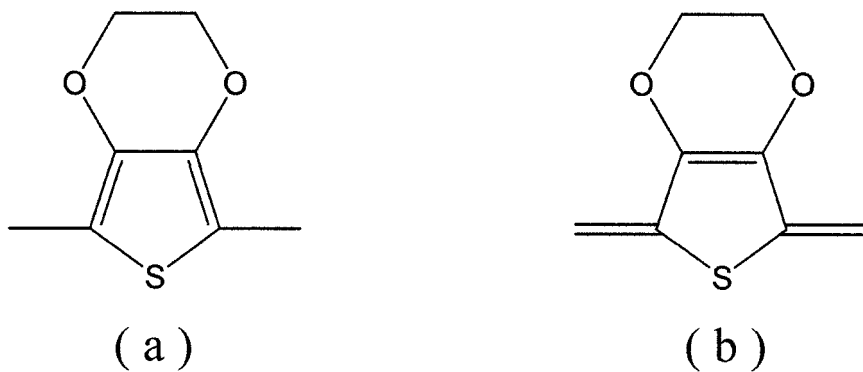
These vibrations are assigned to the  $\text{C}_\alpha=\text{C}_\beta$  symmetric stretching of the five-member thiophene ring on the PEDOT chains.<sup>[12–14]</sup> Two kinds of resonant structures, the benzoid and quinoid structures, have been proposed for PEDOT. (Sch. 1)<sup>[12,13,16]</sup> There are two conjugated  $\pi$ -electrons on the  $\text{C}_\alpha=\text{C}_\beta$  bond in the benzoid structure, and no conjugated  $\pi$ -electron on the  $\text{C}_\alpha-\text{C}_\beta$  bond in the quinoid structure. Thus, the symmetrical  $\text{C}_\alpha=\text{C}_\beta$  stretching vibration will have a red-shift from the benzoid to the quinoid structure. These suggest the transformation of the resonant structure of the PEDOT chain after the conductivity enhancement of the PEDOT : PSS film. Both benzoid and quinoid resonant structures may be present in the untreated PEDOT : PSS film. The benzoid structure may transform into quinoid structure after the treatment, so that the quinoid structure becomes dominant in the high-conductivity E-PEDOT : PSS film. Such resonant structure transformation of PEDOT chains was observed experimentally during the redox processes of PEDOT : PSS film as well.<sup>[12,13]</sup>



**Figure 3.** Raman spectra of (a) high-conductivity E-PEDOT : PSS film and (b) untreated PEDOT : PSS film excited by HeNe laser at 632.8 nm.



**Figure 4.** Deconvolution of the Raman spectra for (a) high-conductivity E-PEDOT : PSS film and (b) untreated PEDOT : PSS film by Lorentzian oscillations.



**Scheme 1.** (a) Benzoid and (b) quinoid structures of a unit of PEDOT.

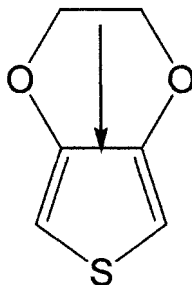


This transformation of the chemical structure of PEDOT chains presumably is due to the conformational change of the PEDOT chains in the PEDOT : PSS film. Coil and linear or expanded-coil conformations have been proposed for the polymer chains in conducting polymers.<sup>[17]</sup> In the coil conformation, the plane of a thiophene ring on the PEDOT chain deviates greatly from the plane of its neighboring thiophene ring, so that the  $C_{\alpha}-C_{\alpha}$  bond between the two thiophene rings is more like a  $\sigma$  bond and has a low density of the conjugated  $\pi$ -electron. Hence, the favored structure is the benzoid structure. In this coil conformation, the conjugated  $\pi$ -electrons are not completely delocalized over the whole PEDOT chain, so that the PEDOT : PSS film will have low charge-carrier mobility. In comparison, in an expanded-coil or linear conformation the neighboring thiophene rings in the PEDOT chains are oriented almost in the same plane, so that the conjugated  $\pi$ -electrons could be delocalized over the whole chain. Thus, the quinoid structure becomes the favored structure. Therefore, resonant structure transformation after the treatment indicates the conformational transformation of PEDOT chains from the coil into the linear or expanded-coil conformation. The PEDOT : PSS chains of expanded-coil or linear conformation have high charge-carrier mobility, and the inter-chain interaction among the PEDOT chains increases after the conformational change. This conformational change is confirmed by the temperature dependence of the conductivity and electron spin resonance (ESR) as well.<sup>[18]</sup>

Hence, the conductivity enhancement is due to the increase of the charge-carrier mobility resulting from the conformational change of the PEDOT chains. Actually, the increase of charge-carrier mobility should be the only reason for the conductivity enhancement, as the mild additive should not change the doping degree of PEDOT : PSS. X-ray photoelectron spectroscopy (XPS) by us, and Kim et al. indicated that the additive has no effect on the XPS of C, S, and O atoms.<sup>[9]</sup>

The interaction between the additive and the PEDOT chains may be the driving force for the conformational change. One common point for polyalcohols and 2-nitroethanol is that they have two or more polar groups in a molecule, and they can form hydrogen bonds to sulfonate or sulfonic acid groups of PEDOT : PSS. Sulfonic acid groups exist in PEDOT : PSS film because the PEDOT : PSS aqueous solution has a pH value of 2. Inganäs et al. also mentioned the possible hydrogen bond between the additive and the polymer.<sup>[6]</sup> The hydrogen bond between the O atoms of PEDOT and the additive should be very weak, as these O atoms connect to a conjugated ring. One polar group of the additive may form a hydrogen bond to the sulfonate or sulfonic acid group of PEDOT : PSS, whereas another polar group may be very close to the PEDOT chain and lead to an interaction between the dipole of this polar group and the dipole moment or the positive charge on the PEDOT chains. Our calculation using the HyperChem program indicates that ethyldioxythiophene has a large dipole moment ( $\mu = 1.87$  D,  $\mu$ : dipole moment) (Sch. 2). This dipole–dipole or dipole–charge interaction may be the driving force for the conformational change of the PEDOT chains. In the case of DMSO, two polar groups (SO and  $SCH_3$ ) can be regarded or the SO group is close to the PEDOT chain after the formation of the hydrogen bond to the sulfonic acid group.

The dipole–dipole or dipole–charge interaction is important only at a very short distance. The hydrogen bond between the additive and the  $PSS^-$  or PSSH chains may be very important for the short distance between the polar group and the PEDOT chain. This is evidenced by the following experiment. The PSSH chains in the PEDOT : PSS



*Scheme 2.* Dipole moment in 3,4-ethylenedioxythiophene.

film were turned into  $\text{PSS}^-$  by treating the film with 0.1 M KOH aqueous solution. Conductivity enhancement by about two orders in magnitude was still observed when this KOH-treated PEDOT : PSS film was treated with EG, but no conductivity enhancement was observed when treated with DMSO. EG can, whereas DMSO cannot, form a hydrogen bond to  $\text{PSS}^-$ . This supports our statement about the role of the hydrogen bond for the conductivity enhancement.

This dipole–dipole or dipole–charge interaction may not happen in aqueous solution, as no conductivity enhancement occurs for the E-PEDOT : PSS film dried at room temperature. Further evidence is that no characteristic peak was observed for the untreated and treated PEDOT : PSS films. This conformational change of the PEDOT chains in the film may make the backbone pack better, but does not significantly increase the crystallization of the film, so it cannot be detected by x-ray diffraction. This is different from the “secondary doping” of polyaniline.<sup>[17]</sup> The solvent could affect the conformation of polyaniline chains in solution, so that highly crystalline polyaniline film can be formed when an appropriate solvent is selected.

The conformational change sometimes can be observed by UV-Visible spectroscopy, such as the secondary doping of polyaniline. Inganäs et al. observed small changes optically on the UV-Visible absorption spectra between the high- and low-conductivity PEDOT : PSS films,<sup>[6]</sup> but we did not observe any significant difference in the UV-Visible spectra from 200 to  $2600\text{ cm}^{-1}$ . The untreated PEDOT : PSS already had a strong band corresponding to the bipolaron in the infrared range, as some PEDOT chains have a linear or expanded-coil conformation. This strong band may hide the effect of the conformational change on the absorption spectrum. This is different from the secondary doping of polyaniline. The dominant conformation is the coil structure for low conductivity polyaniline film and is the linear or expanded-coil conformation after secondary doping.<sup>[17]</sup> Thus, a remarkable effects of secondary doping can be observed in the UV-Visible absorption spectra of polyaniline.

### **Application of High-Conductivity PEDOT : PSS in Polymer Optoelectronic Devices**

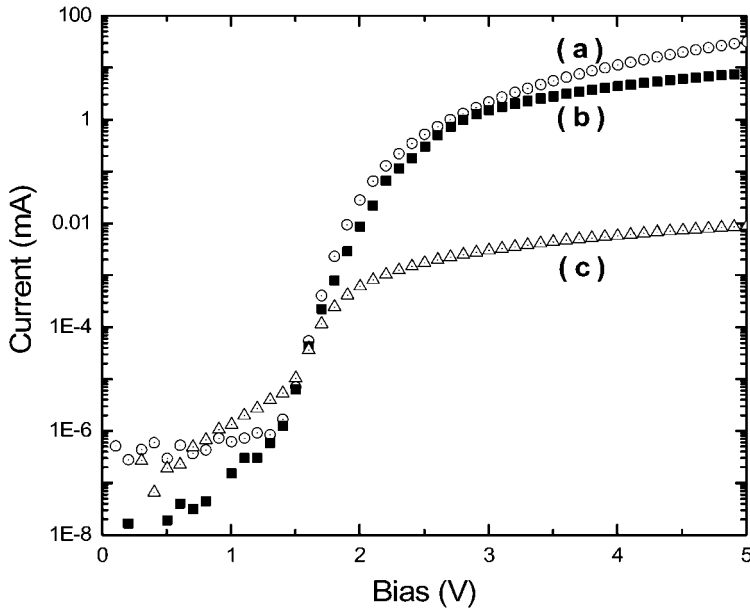
No significant difference was observed in the UV-Visible spectra of the high-conductivity PEDOT : PSS film and untreated PEDOT : PSS film. The high-conductivity

PEDOT:PSS film remains highly transparent in the visible range. One direct application for high-conductivity PEDOT:PSS film is as the anode in organic light-emitting diodes and PVs. Table 1 lists the conductivity of ITO, untreated and treated-PEDOT film. Our treated PEDOT:PSS films have conductivity and transparency comparable with the best PEDOT:PSS provided by Agfa Company (see, website: <http://www.agfa.com/sfc/polymer>). PLEDs were fabricated using EG-PEDOT:PSS film with a thickness of about 300 nm as the anode on glass substrates. The light-emitting layer is MEH-PPV film and the cathode is Ca/Al. Figures 5 and 6 show the current-voltage ( $I$ - $V$ ) and the luminance-voltage ( $L$ - $V$ ) curves, respectively, for such a device. The performance of the devices using ITO/PEDOT:PSS or PEDOT:PSS films are also presented for comparison. The turn-on voltage is the same for ITO/PEDOT:PSS, EG-PEDOT:PSS, or PEDOT:PSS films being used as the anode. This is because the resistance of the MEH-PPV layer is much higher than the anode before turn-on of the device, and the poly-alcohol may have no effect on the work function of the PEDOT:PSS film. The device using EG-PEDOT:PSS film as the anode exhibits a current density very close to that using ITO/PEDOT:PSS as the anode. This current is almost three orders in magnitude higher than the device using PEDOT:PSS film as the anode. At a constant current of 3 mA, the PLED using EG-PEDOT:PSS film as the anode emits light homogeneously as in case of ITO/PEDOT:PSS as the anode. In contrast, the PLED using the untreated PEDOT:PSS film as the anode emits light inhomogeneously, and moreover a weak light signal can only be observed at the edge of the device at a voltage of 80 V. The luminance of PLED using EG-PEDOT:PSS film of 300 nm thickness as the anode is almost half as that of the device using ITO/PEDOT:PSS as the anode. This is because the EG-PEDOT:PSS film of 300 nm thickness has a low transmission in the visible range. When the device was fabricated using EG-PEDOT:PSS film of 100 nm as the anode, the device exhibits luminance of 200 cd/m<sup>2</sup> and efficiency of 1.2 cd/A at a constant current of 3 mA, which is comparable with that using ITO/PEDOT:PSS as the anode.

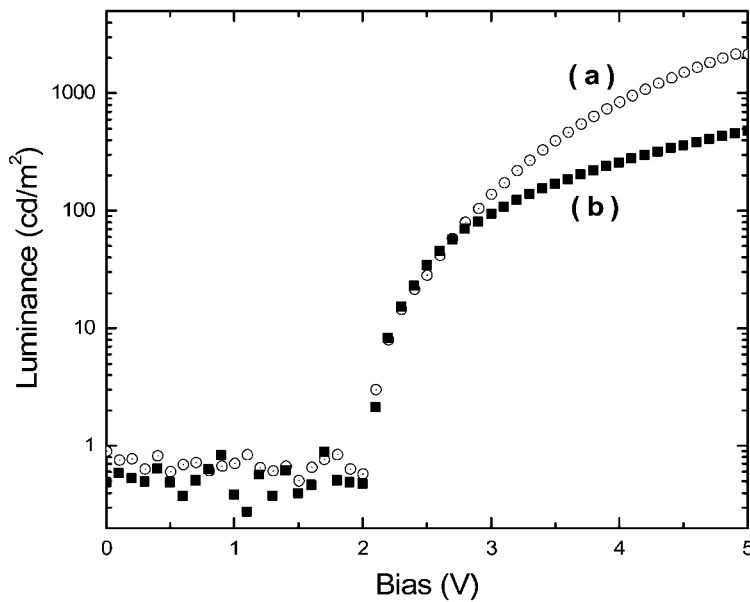
E-PEDOT:PSS film formed by spin-coating PEDOT:PSS aqueous solution added with *meso*-erythritol on glass substrate and subsequently baked at 150°C for 1 hr was used as the anode to construct polymer PVs. The active layer used is a blend of MEH-PPV and PCBM, and the cathode is Ca/Al. Figure 7 shows the  $I$ - $V$  characteristics of the device under 100 mW/cm<sup>2</sup> AM1.5G illumination. The device with PEDOT:PSS layer of 250 nm exhibits high performance: short-circuit current ( $I_{sc}$ ) of 5.1 mA/cm<sup>2</sup>, open-circuit voltage of 0.74 V, and power efficiency of 1.5%. These performances are very close to those of the devices using ITO/PEDOT:PSS as the anode. Our PLEDs

**Table 1.** Conductivity of ITO, untreated PEDOT:PSS and treated PEDOT:PSS films.

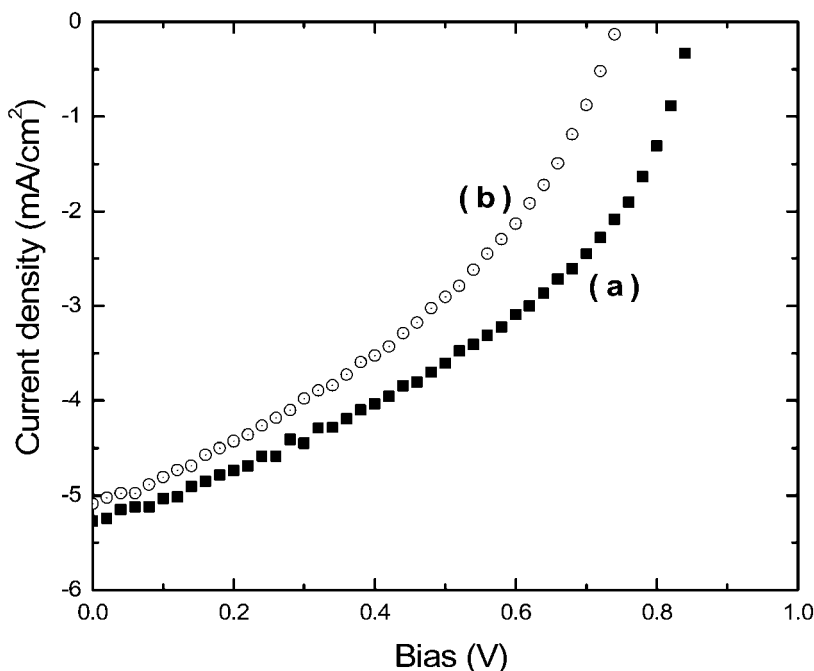
Materials	Conductivity (S/cm)
ITO	4000
PEDOT:PSS	0.4
EG-PEDOT:PSS	160
E-PEDOT:PSS	155



**Figure 5.** Current–voltage curves of PLEDs: glass/anode/MEH-PPV/Ca/Al using (a) ITO/untreated PEDOT:PSS (40 nm in thickness), (b) EG–PEDOT:PSS (300 nm in thickness), and (c) untreated PEDOT:PSS (300 nm in thickness) as the anode.



**Figure 6.** Luminance–voltage curves of PLEDs: glass/anode/MEH-PPV/Ca/Al using (a) ITO/untreated PEDOT:PSS (40 nm in thickness) and (b) EG–PEDOT:PSS (300 nm in thickness) as the anode.



**Figure 7.** Current–voltage curves of PVs: glass/anode/MEH-PPV:PCBM/Ca/Al using (a) ITO/untreated PEDOT:PSS (40 nm in thickness) and (b) high-conductivity E-PEDOT:PSS (250 nm in thickness) as the anode. A  $100\text{ mW/cm}^2$  AM1.5G simulated solar illumination was used from the anode side.

and PVs using the high-conductivity PEDOT:PSS film as the anode have higher performance than similar devices fabricated by other researchers.<sup>[8,11]</sup>

## CONCLUSIONS

In conclusion, we demonstrated that the conductivity of PEDOT:PSS films were enhanced by more than two orders in magnitude by adding compounds of two or more polar groups into the PEDOT:PSS aqueous solution. The addition of additive dramatically increases the conductivity while maintaining the optical transparency of the modified polymer films. Our results show that it is feasible to use processable conducting polymer as anodes for fabricating polymer optoelectronic devices. Comparing with ITO anodes, PEDOT:PSS anodes acquire the potential to fabricate lower cost and more mechanically flexible devices.

## ACKNOWLEDGMENT

This research was financially supported by the Air Force Office of Scientific Research, Program Director, Dr. Charles Lee.

## REFERENCES

1. Friend, R.H.; Gymer, R.W.; Holmes, A.B.; Burroughes, J.H.; Marks, R.N.; Taliani, C.; Bradley, D.D.C.; Dos Santos, D.A.; Bredas, J.L.; Logdlund, M.; Salaneck, W.R. Electroluminescence in conjugated polymers. *Nature* **1999**, *397*, 121.
2. Heywang, G.; Jonas, F. Poly(alkylenedioxythiophene)s-new, very stable conducting polymers. *Adv. Mater.* **1992**, *4*, 116.
3. Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J.R. Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future. *Adv. Mater.* **2000**, *12*, 481.
4. Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A.J. Polymer light-emitting diodes with polyethylene dioxythiophene–polystyrene sulfonate as the transparent anode. *Synth. Met.* **1997**, *87*, 171.
5. Bharathan, J.; Yang, Y. Polymer electroluminescent devices processed by inkjet printing: I. Polymer light-emitting logo. *Appl. Phys. Lett.* **1998**, *72*, 2660.
6. Pettersson, L.A.A.; Ghosh, S.; Inganäs, O. Optical anisotropy in thin films of poly(3,4-ethylenedioxythiophene)–poly(4-styrenesulfonate). *Org. Electron.* **2002**, *3*, 143.
7. Ghosh, S.; Inganäs, O. Nano-structured conducting polymer network based on PEDOT-PSS. *Synth. Met.* **2001**, *121*, 1321.
8. Zhang, F.; Johansson, M.; Anderson, M.R.; Hummelen, J.C.; Inganäs, O. Polymer photovoltaic cells with conducting polymer anodes. *Adv. Mater.* **2002**, *14*, 662.
9. (a) Kim, J.Y.; Jung, J.H.; Lee, D.E.; Joo, J. Enhancement of electrical conductivity of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) by a change of solvents. *Synth. Met.* **2002**, *126*, 311; (b) Lee, C.S.; Kim, J.Y.; Lee, D.E.; Koo, Y.K.; Joo, J.; Han, S.; Beag, Y.W.; Koh, S.K. Organic based flexible speaker through enhanced conductivity of PEDOT/PSS with various solvents. *Synth. Met.* **2003**, *13*, 135–136.
10. Jönsson, S.K.M.; Birgersson, J.; Crispin, X.; Greczynski, G.; Osikowicz, W.; van der Gon, A.W.D.; Salaneck, W.R.; Fahlman, M. The effects of solvents on the morphology and sheet resistance in poly(3,4-ethylenedioxythiophene)–polystyrene-sulfonic acid (PEDOT–PSS) films. *Synth. Met.* **2003**, *139*, 1.
11. (a) Kim, W.H.; Mäkinen, A.J.; Nikolov, N.; Shashidhar, R.; Kim, H.; Kafafi, Z.H. Molecular organic light-emitting diodes using highly conducting polymers as anodes. *Appl. Phys. Lett.* **2002**, *80*, 3844; (b) Kim, W.; Mäkinen, A.J.; Nikolov, N.; Shashidhar, R.; Kim, H.; Kafafi, Z.H. Molecular organic light emitting diodes using highly conductive and transparent polymeric anodes. *Proceedings of SPIE* **2002**, *4464*, 85; (c) Mäkinen, A.J.; Kim, W.H.; Hill, I.G.; Shashidhar, R.; Nikolov, N.; Kafafi, Z.H. Hole Injection energetics at highly conducting polymer anode: small molecule interfaces studied with photoemission spectroscopy. *Proceedings of SPIE* **2002**, *172*, 4464.
12. Garreau, S.; Duvail, J.L.; Louarn, G. Spectroelectrochemical studies of poly(3,4-ethylenedioxythiophene) in aqueous medium. *Synth. Met.* **2002**, *125*, 325.
13. Łapkowski, M.; Proń, A. Electrochemical oxidation of poly(3,4-ethylenedioxythiophene)—“*in situ*” conductivity and spectroscopic investigations. *Synth. Met.* **2000**, *79*, 110.
14. Garreau, S.; Louarn, G.; Buisson, J.P.; Froyer, G.; Lefrant, S. *In situ* spectroelectrochemical Raman studies of poly(3,4-ethylenedioxythiophene) (PEDT). *Macromolecules* **1999**, *32*, 6807.

15. da Silva, J.E.P.; Temperini, M.L.A.; de Torresi, S.I.C. Secondary doping of polyaniline studied by resonance Raman spectroscopy. *Electrochim. Acta* **1999**, *44*, 1887.
16. Dkhissi, A.; Louwet, F.; Groenendaal, L.; Beljonne, D.; Lazzaroni, R.; Brédas, J.L. Theoretical investigation of the nature of the ground state in the low-bandgap conjugated polymer, poly(3,4-ethylenedioxythiophene). *Chem. Phys. Lett.* **2002**, *359*, 466.
17. McDiarmid, A.G.; Epstein, A.J. *Mat. Res. Soc. Symp. Proc.* **1994**, *318*, 133.
18. Ouyang, J.; Xu, Q.; Chu, C.W.; Yang, Y.; Li, G.; Shinar, J. manuscript in preparation.