Alkoxysulfonate-Functionalized PEDOT Polyelectrolyte Multilayer Films: Electrochromic and Hole Transport Materials

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Received December 19, 2004; Revised Manuscript Received February 2, 2005

ABSTRACT: Water-soluble poly(4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid (PEDOT-S) has been synthesized both chemically and electrochemically, and the properties of the resultant films have been examined and compared. In particular, it was found that PEDOT-S, deposited in conjunction with poly(allylamine hyrochloride) PAH in the form of polyelectrolyte multilayer (L-B-L) films of PEDOTS/PAH, possesses highly advantageous properties that allow for applications involving aqueous-based electrolytes. Electrochemically prepared films of PEDOT-S and L-B-L prepared films of PEDOT-S/PAH were characterized by electrochemical, spectroelectrochemical, and colorimetric methods illustrating reversible redox states at −0.2 and +0.2 V, respectively (vs Ag/Ag$^+$ in organic media), which resulted in distinctive color changes between light blue (oxidized) and purple/pink (neutral). The change in color states was evident by a change in the electronic absorbance in the 500 nm region (neutral state) which was transferred to the near-IR absorption >800 nm (oxidized state). The phenomena of "acid doping" in aqueous and organic media was also investigated spectroscopically and found to result in a reversible color change accompanied by a relatively small changes in conductivity between 2×10^{-4} S/cm (oxidized) and 7.1×10^{-5} S/cm (neutral) when films were deposited on glass. In all cases, PEDOT-S/PAH exhibited superior and more reproducible electrochemical properties relative to electrochemically formed films that were tested for possible application in electrochromic devices and as the hole transport layer of OLEDs. It was found that PEDOT-S/PAH displays comparable properties to spin-coated PEDOT:PSS as a hole injecting layer in NIR emitting PLEDs.

Introduction

The significance and impact of poly(3,4-ethylenedioxythiophene) PEDOT and its derivatives in the field of conducting polymers have been discussed at length in several recent reviews.[1,2] It displays a high contrast in color between the oxidized, highly transmissive state and the deep blue neutral state,[3,4] making it well suited for electrochromic applications. The impressive conductivity (up to ca. 300 S/cm) of PEDOT and its commercial availability in the form of PEDOT/PSS have also led to its incorporation into LEDs as a hole transport layer.[5] The synthesis of conjugated polymers in a form that can be easily processed in aqueous media has been one of the major challenges in this field and has stimulated progress in the commercial arena. The commercialization of PEDOT/PSS is largely due to its proccessable nature; therefore, the ability to chemically and electrochemically synthesize fully water-soluble PEDOT derivatives such as poly(4-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-2-yl-methoxy)-1-butanesulfonic acid (PEDOT-S) greatly increases its versatility for deposition and application.

Covalently linking an ionic moiety such as a sulfonate,[6] carboxylate,[7] or phosphonate[8] to the β-position of thiophene results in water-soluble and self-dopable polymers, where the dopant ion is attached to the polymer backbone. The self-doping process is accompanied by the expulsion of charge balancing cations from the film upon oxidation of the polymer, and charge neutraliztion leads to their reinclusion into the film, as first demonstrated by Wudl et al.,[9] followed by the Reynolds group.[10] The presence of the dopant anion on the polymer chain was thought to potentially initiate faster switching within the polymer film. PEDOT-S was first synthesized electrochemically by Chevrot et al.[11] as a copolymer with EDOT, and recently Kumar et al.[12] have reported the successful electrochemical polymerization of PEDOT-S as a homopolymer in a mixture of organic/aqueous media. Zotti et al.[13] also reported the successful electrochemical synthesis of PEDOT-S in highly acidic solutions as well as the first chemical synthesis by oxidative polymerization induced by ferric tosylate.

Advantages in the proccessability of chemically polymerized, water-soluble polythiophene derivatives have been recognized by a number of researchers in this field.[14] Chemical polymerization enables the deposition of films on substrates by a variety of methods such as casting and spin-coating or through the use of Langmuir−Blodgett and polyelectrolyte multilayer deposition techniques. Decher et al.[15,16] were the first to employ the layer-by-layer (L-B-L) deposition of water-soluble polyelectrolyte polymers, as summarized in our prior communication on this work.[17] Zotti et al.,[18] who were the first to implement the layer-by-layer deposition of all polythiophene multilayer films, have employed this method of film deposition extensively, along with pioneering work by others such as Rubner et al.[19] Lukkari et al.[20,21] have also reported the synthesis of all polythiophene-based multilayer films, where both the film deposition and characterization were carried out in aqueous media.

In a prior communication, we reported the layer-by-layer deposition of PEDOT-S polyelectrolyte in conjunction with PAH.[17] The homogeneous film quality and self-healing deposition characteristics for layer-by-layer conjugated polyelectrolytes have proven useful in de-

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10.1021/ma047396+ CCC: $30.25

positing light-emitting films in LEDs[22] and films for electrochromic devices.[17,23] The ability to control the porosity of films prepared during the deposition process, by adjusting the ionic strength of the electrolyte, results in efficient switching of multilayer electroactive polymer films, a property that lends itself well to electrochromic applications.[24,25]

Here, we report the chemical synthesis of water-soluble, self-doped PEDOT-S. The electrochemical and spectroelectrochemical properties of PEDOT-S, synthesized chemically and deposited as multilayer films in water, are compared with PEDOT-S homopolymer films electrochemically deposited in organic/aqueous solvent mixtures. Multilayer films were characterized in aqueous and organic media, whereas electrochemically synthesized homopolymer films of PEDOT-S could only be characterized in organic solvents. Unusual acid doping behavior observed for both electrochemically deposited PEDOT-S and PEDOT-S/PAH films is reported and compared to the electrochemical oxidation and charge neutralization of the polymer films. PEDOT-S and PEDOT-S/PAH films are shown to possess distinct fast switching electrochromic properties that are enhanced when films are deposited using the layer-by-layer deposition techniques. This also allows PEDOT-S/PAH to be employed as an effective hole transport layer in PLEDs.

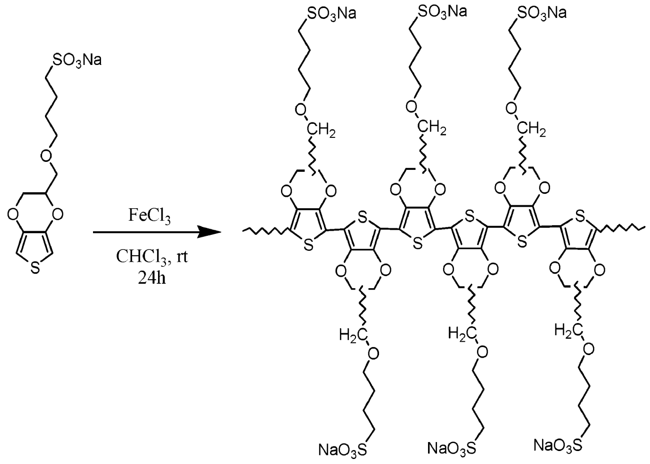
Experimental Section

Chemical Synthesis of PEDOT-S. The 4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid, sodium salt (EDOT-S), monomer was synthesized according to a synthetic procedure described in the literature.[11] EDOT-S (0.1 g, 0.3 mmol) and 3.3 equiv of iron(III) chloride were mixed in 15 mL of chloroform. The reaction was carried out under argon at room temperature over 24 h. The solution was then poured into 100 mL of methanol, in which a few drops of hydrazine was added. After filtration, the dark precipitate was stirred in a 1 M sodium hydroxide methanolic solution (200 mL) for 2 days in order to exchange the iron complexed with the sulfonate groups for sodium ions. The solution was filtered again, and the black polymer powder was stirred in 200 mL of deionized water for 1 day and then filtered again. The polymer was then precipitated in acetone and dried under vacuum. Finally, the polymer was dialyzed with deionized water for 3 days using a 3500 g/mol cutoff membrane prior to use.

Electrochemistry. Polymer films were synthesized onto ITO glass or Pt working electrodes using a three-electrode cell, comprising a Pt auxiliary electrode and an Ag/AgCl reference electrode when in aqueous electrolytes, or a Ag/Ag$^+$ in organic media. Homopolymer PEDOT-S films were synthesized from EDOT-S (0.01 M) solutions in $LiClO_4$(0.1 M)/propylene carbonate (PC) with 5% water by either repeated voltammetric scanning or the application of a constant potential. Homopolymer characterization was carried out in $LiBF_4$ (0.1 M)/acetonitrile monomer free electrolyte solution using 5% water with Ag/Ag$^+$ as the reference. Polyelectrolyte multilayer films were characterized in Na_2SO_4(0.2 M)/deionized water with an Ag/AgCl electrode as well as in $LiBF_4$ (0.1 M)/acetonitrile organic electrolyte solution.

Multilayer Film Deposition. PEDOT-S was synthesized as stated, and poly(allylamine hydrochloride) (PAH) with M_w ca. 70 000 g mol^{-1} was purchased from Aldrich and used without further purification. Polymers and electrolyte solutions were made using Milli-Q 18 MΩ (Millipore) water and Na_2SO_4 (0.2 M) (Aldrich). Polymer concentrations were based on the monomer, PAH (0.01 M) and PEDOT-S (0.02 M); the pH of both solutions was adjusted to ~2.8 with perchloric acid. Substrates were unmodified ITO glass, $R_s = 8-12$ Ω/sq (Delta Technologies), that was cleaned using an ultrasonicator bath in water and then acetone prior to use. Film assembly was automated using a modified Carl Zeiss HMS DS-50 slide stainer. Substrates were submerged in each polyelectrolyte solution for 15 min followed by agitation for 1 min in two separate Milli-Q water baths. Monitoring of film deposition was carried out on a Hewlett-Packard 8452A diode array spectrophotometer. Spectroelectrochemistry was performed in-situ on a Cary 500 UV−vis−NIR spectrophotometer with Ag wire as a quasi-reference electrode and Pt wire as the counter electrode. Coloration efficiencies were carried out using the kinetics mode on the Cary 500 UV−vis−NIR spectrophotometer. Electrochemical and spectroelectrochemical analysis of the films was controlled by an EG&G Princeton Applied Research model 273 A potentiostat/galvanostat, in a three-electrode cell, with Ag/AgCl as the reference electrode and a platinum flag as the counter electrode. Film thicknesses were measured using a Sloan Dektak II profilometer, and conductivity measurements were carried out using the four-point probe method.

Scheme 1



Colorimetry measurements were obtained by the use of a Minolta CS-100 Chroma Meter, and CIE recommended normal/normal (0/0) illuminating viewing geometry for transmittance measurements. The samples were illuminated from behind by a D50 (5000 K) light source in a light booth specially designed to exclude external light. A background measurement was taken using a piece of blank ITO in an electrolyte solution of either Na_2SO_4(0.2 M)/H_2O or $LiBF_4$(0.1 M)/acetonitrile, in a standard quartz cuvette.

Near-IR-LED Construction. Near-IR electroluminescent devices were constructed beginning with cleaned ITO glass coated with PEDOT-S or PEDOT/PSS (Bayer Baytron P VP Al 4083) as a hole transport layer. A 10 mol % PPP−OR11:Yb(DNM)$_3$phen blend was spin-coated from solution in which the composition (mol %) of the lanthanide complex is based on polymer repeat unit. The resulting film was dried under vacuum (1×10^{-6} Torr) for 16 h at room temperature. Calcium (50 Å) followed by Al (2000 Å) layers were thermally evaporated at 4×10^{-7} Torr without breaking the vacuum between metal depositions. After deposition, the device was encapsulated with epoxy under an argon atmosphere to minimize exposure to oxygen and moisture. All device measurements were made at room temperature.

Results and Discussion

Polymer Synthesis and Characterization. EDOT-S was synthesized in an eight-step procedure as previously described by Chevrot et al.[11] and subsequently polymerized with $FeCl_3$ in chloroform,[26] to give the nominal structure shown in Scheme 1 after neutralization. The polymer is obtained in a partially doped form where some of the pendant sulfonate ions serve as dopants and the others give the polymer its polyelectrolyte nature. After dialysis (3500 g/mol cutoff mem-

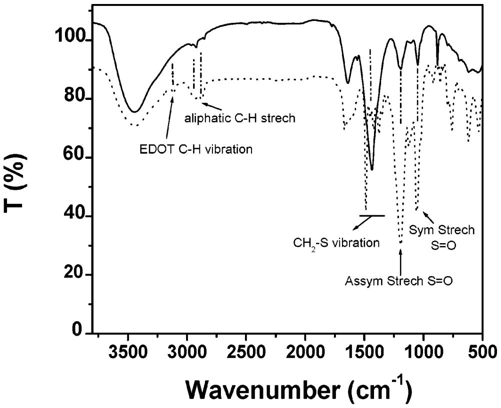


Figure 1. FT-IR spectra of the monomer EDOT-S (dashed line) and the polymer PEDOT-S (solid line).

brane), the polymer (black powder) was fully solubilized in water to give a dark brown solution characteristic of the partially oxidized state of the polymer. The color of the solution shifts to dark purple when the polymer is charge neutralized and light blue when it is fully oxidized. The polymer was characterized by solid-state NMR, UV−vis, and FT-IR. Solid-state ^{13}C NMR was obtained as opposed to solution NMR due to poor resolution of the spectrum in D_2O as was also seen by Kumar for electrochemically prepared polymer.[12] The solid state NMR showed broad peaks centered around 20, 30, 50, 70, 110, and 140 ppm, which correlate appropriately with the peaks seen in the ^{13}C NMR of the monomer, indicating that the repeat unit is as expected and no degradation is occurring during polymerization. The FT-IR spectra of both EDOT-S and the polymer are shown in Figure 1. The band at 2987 cm^{-1} is characteristic of the EDOT α C−H vibration of the EDOT-S and disappears completely upon polymerization. The presence of the symmetric and asymmetric S=O stretching modes in both monomer and polymer is consistent with the proposed structures and stability of the pendant chains to the polymerization conditions. The polymerization of EDOT-S is supported by an observed red shift of the $\pi-\pi^*$ transition upon polymerization as seen in UV−vis spectra. While direct molecular weight determination was not possible, the dialysis procedure used in purification removed short chain oligomers. The polymeric nature of the material is also evident in the optical properties where the polymer has a low electronic band gap (as discussed below). Thermogravimetric analysis (TGA) of PEDOT-S was carried out under nitrogen and showed that the polymer remains stable up to 290 °C, after which rapid weight loss is observed as the polymer degrades.

Layer-by-Layer Deposition of PEDOT-S/PAH Films. As we have previously reported,[17] PEDOT-S/PAH multilayer films can be deposited on ITO-coated glass by alternately dipping the substrate into solutions containing polyelectrolytes dissolved in Na_2SO_4 (0.2 M)/H_2O at a pH of ~2.8. Between each consecutive submersion process, the substrate was thoroughly rinsed with deionized water. The positively charged polyelectrolyte PAH was adsorbed first, enabling the sequential deposition of polyelectrolyte films onto the ITO glass substrate (possessing a negative polarity). Multilayer films were also successfully deposited onto regular glass slides in order to facilitate conductivity measurements.

L-B-L films of PEDOT-S and PAH were deposited in the oxidized (blue) state, as the pH of the electrolyte solution appears to be sufficient to dope the polymer. PEDOT-S remains in its doped form throughout multilayer deposition as evidenced by UV−vis spectroscopy. Depositing the neutral polymer, as opposed to the oxidized form, was found to result in much thinner films, as was observed by Lukkari et al.[20,27] during the fabrication of multilayer films of a sulfonated polythiophene. The deposition of multilayer films was monitored by UV−vis spectroscopy and cyclic voltammetry. Films were sufficiently thick to be studied by profilometry, and as expected, there was a linear correlation between the number of bilayers deposited, the UV−vis absorbance, and the thickness of the multilayers as seen in Figure 2. The absorbance of the film is an accurate method of monitoring the amount of polymer deposited for each bilayer (BL). It allows for the precise control of film thickness by the deposition of a given number of PEDOT-S layers at an incremental absorbance increase of 0.011 per bilayer and thickness increase of 44 Å per bilayer.

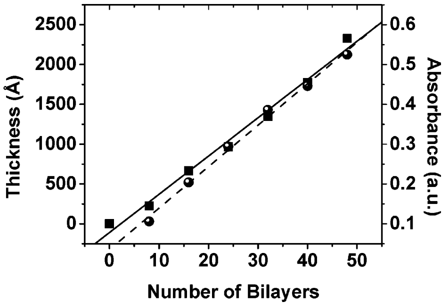


Figure 2. PEDOT-S/PAH L-B-L film thickness (solid line) and optical absorbance (dashed line) as a function of the number of bilayers deposited.

Electrochemical Polymerization. To enable the comparison of L-B-L and electrochemically deposited PEDOT-S films, the electrochemical synthesis of PEDOT-S was carried out by galvanostatic, potentiostatic, and potentiodynamic methods on both platinum and ITO-coated glass substrates. In contrast with work carried out by Zotti et al.,[13] polymer films were deposited under nonacid conditions. The preferred method of polymer synthesis for optimum film formation was the application of a constant potential of 0.9 V in an electrolyte solution of $LiClO_4$ (0.1 M)/ propylene carbonate (PC), with 5% water to dissolve the EDOT-S. The deposition of PEDOT-S was found to proceed slowly, and the synthesis of thick PEDOT-S films was difficult even when the applied potential was increased to 1.1 V (vs Ag/Ag^+). This may support suggestions by Zotti et al.[13] for the need to mediate the acid scavenging nature of the sulfonate moiety.

The synthesis of PEDOT-S by repeated voltammetric scanning between 0 and 1.1 V (vs Ag/Ag^+) at scan rates between 2 and 50 mV/s produced thin, light blue electroactive films. The monomer peak oxidation potential of EDOT-S was observed to be ~0.9 V (vs Ag/Ag^+). The cyclic voltammogram of EDOT-S is unusual in that, although an electroactive polymer is deposited onto the electrode surface over consecutive cycles, the current response decreases and no polymer redox response is observed. The lack of redox response during polymer synthesis is probably due to poor cation mobility within the polymer film in the PC-based electrolyte, even when PEDOT-S was synthesized at scan rates as slow at 2 mV/s.

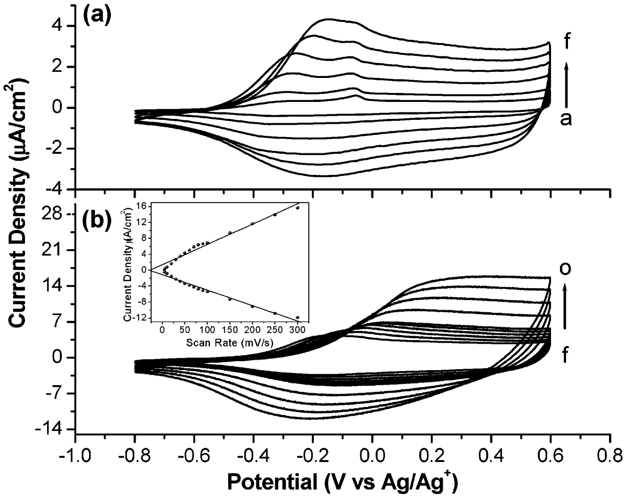


Figure 3. Cyclic voltammograms of PEDOT-S deposited electrochemically at scan rates between (a) 5−50 mV/s for curves a−f and (b) 50−300 mV/s for curves f−o in $LiBF_4$(0.01 M)/acetonitrile (5% water). Inset: current density as a function of scan rate for full experiment.

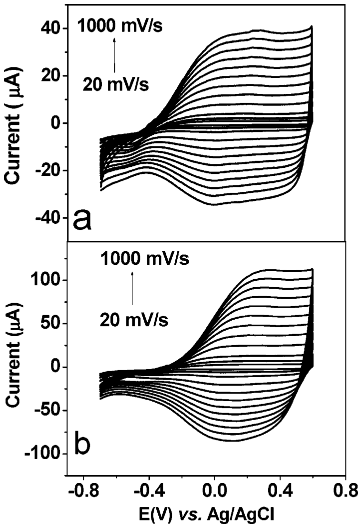


Figure 4. Scan rate dependence of an (a) 10 BL and (b) 50 BL PEDOT-S/PAH film in Na_2SO_4 (0.2 M)/ H_2O.

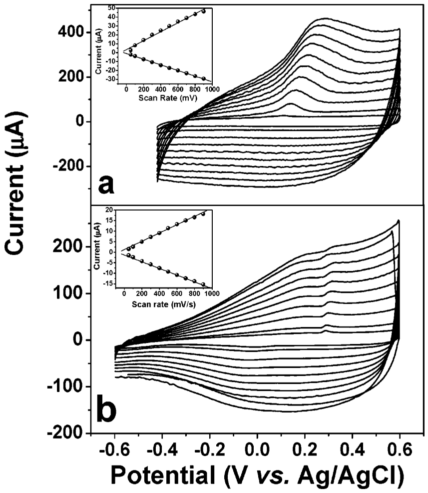


Figure 5. Scan rate dependence of a 30 BL PEDOT-S/PAH film at scan rates between 50 and 900 mV/s in (a) $LiBF_4$ (0.01 M)/acetonitrile and (b) Na_2SO_4 (0.2 M)/ H_2O.

Electrochemical Characterization of PEDOT-S and PEDOT-S/PAH Films. The electrochemical characteristics of electrochemically synthesized PEDOT-S were investigated in 0.1 M $LiBF_4$ in acetonitrile with 5% water and resulted in well-defined redox behavior of the polymer films at scan rates up to 50 mV/s (Figure 3a), while broader redox peaks were observed at scan rates up to 300 mV/s (Figure 3b). The redox processes for the electrochemically deposited polymer are centered around −0.2 V vs Ag/Ag^+ at 50 mV/s. This oxidation potential is considerably less than that of the poly(3-thiophenebutanesulfonate) (~0.75 V vs Ag/Ag^+), demonstrating the benefit of the dioxy substitution pattern on the thiophene ring.[9] The polymer is light transmissive blue in the oxidized state and purple/pink in its neutral state.

A range of acetonitrile and propylene carbonate based electrolyte solutions were investigated, but with the exception of $LiBF_4$, PEDOT-S tended to exhibit poor redox properties unless scan rates were less than 10 mV/s and 5% water was added to the electrolyte. The size of the cation is important due to its expulsion and reincorporation into the polymer during the oxidation and charge neutralization processes as the polymer electrochemistry proceeds via a cation-dominated self-doped mode. Li^+ gave the fastest redox response, while the electronic activity with TBA^+ was negligible. The scan rate dependence for switching the electrochemically deposited polymer in $LiBF_4$ suggests that the polymer redox response is non-diffusion-limited up to a scan rate of 300 mV/s as the current response scales linearly with scan rate (Figure 3b, inset) though there is a positive potential shift in the oxidation potential at the faster scan rates. The addition of 5% water to the electrolyte solution is crucial in obtaining reproducible electrochemistry; however, increased water content in the electrolyte begins to dissolve the electrochemically deposited homopolymer. This optimization of solution dielectric properties allows solvation of the film, inducing ion transport without dissolution.

We have recently communicated the electrochemical switching of PEDOT-S/PAH multiplayer films as a function of the number of bilayers deposited in Na_2SO_4 (0.2 M)/H_2O.[17] In this present work, scan rate dependence studies were carried out on films ranging between 5 and 50 BLs, as seen in Figure 4 for the 10 and 50 BL films, and were found to display fast switching redox responses with currents that are linear with scan rate through the range of film thickness. The scan rate dependence of multilayer films in different solvents was also investigated. Figure 5 shows the cyclic voltammetric response and scan rate dependence of a single 40 BL PEDOT-S/PAH film examined first in aqueous (Figure 5b) and subsequently in acetonitrile electrolyte (Figure 5a). The reference electrodes were Ag/Ag^+ and Ag/AgCl for the organic and aqueous electrolytes, respectively, but the potentials reported in Figure 5 were referenced to a Ag/AgCl reference electrode using ferrocene. In both $LiBF_4$ (0.1 M)/acetontrile and Na_2SO_4 (0.2 M)/H_2O the oxidation peak of PEDOT-S/PAH is between 0.2 and 0.3 V vs Ag/AgCl. The scan rate dependence of PEDOT-S/PAH in organic and aqueous electrolyte is non-diffusion-limited to a scan rate of at least 900 mV/s. From this it is clear that PEDOT-S/PAH deposited from water is electroactive in both aqueous and organic media. The redox switching of PEDOT-S/PAH in both media is stable at much higher scan rates than the PEDOT-S homopolymer prepared electrochemically. This can be attributed to a high degree of integrity

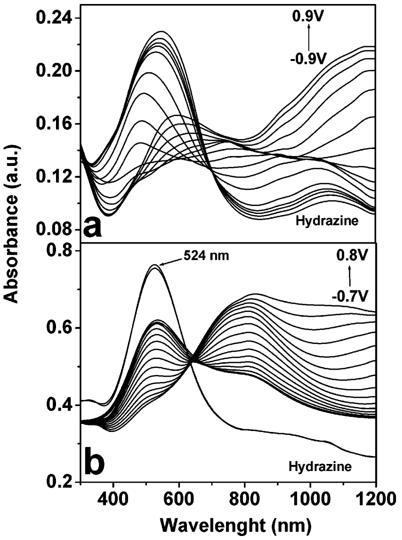


Figure 6. Spectroelectrochemistry in $LiBF_4$ (0.1 M)/ACN of (a) PEDOT-S electrochemically deposited and (b) PEDOT-S/PAH.

of the multilayer films which allows for good contact to the electrode and greater cation mobility.[28] Other methods of PEDOT-S deposition were attempted, including solution-casting and spin-coating, but these films yielded poor electrochemical response, even after the addition of 5% water to the electrolyte solution.

Spectroelectrochemistry. The spectroelectrochemistry of electrochemically prepared PEDOT-S (Figure 6a) was compared with a 32 BL film of PEDOT-S/PAH, in $LiBF_4$ (0.1 M)/acetonitrile (Figure 6b). The spectroelectrochemistry of PEDOT-S/PAH in aqueous media has previously shown that the homogeneous quality of these films allows for a very reproducible transition between the oxidized and neutral states, regardless of the number of bilayers deposited.[17] This is now also shown to be true when multilayer films were switched in organic electrolytes as illustrated in Figure 6b. The neutral multilayer PEDOT-S/PAH film (full neutralization attained with hydrazine treatment) undergoes a clean and homogeneous transition to the oxidized state through an isosbestic point upon oxidation. A distinct color change results, and the films switch from purple/pink to light blue as the $\pi-\pi^*$ absorbance (524 nm) decreases and gives way to charge carrier bands at 800 and 1240 nm.

The spectroelectrochemistry of electrochemically prepared PEDOT-S is more complicated than that of the multilayer films as evidenced by comparison of the two spectral series. As with the multilayer film, the PEDOT-S oxidized form exhibits full depletion of the $\pi-\pi^*$ transition and an increase in the charge carrier absorbance at longer wavelengths. However, at higher oxidation potentials as the NIR absorption maximizes, an additional band appears at 610 nm that increases at higher doping levels, which is not present during the oxidation of L-B-L films. This feature has been observed previously in poly(spiro-BiProDOT) and is attributed to cation-radical (polaron) states that are induced on portions of the polymer chair with short conjugation lengths.[29] As the PEDOT-S prepared chemically is purified by dialysis, short oligomers are removed and are not present in the final film.

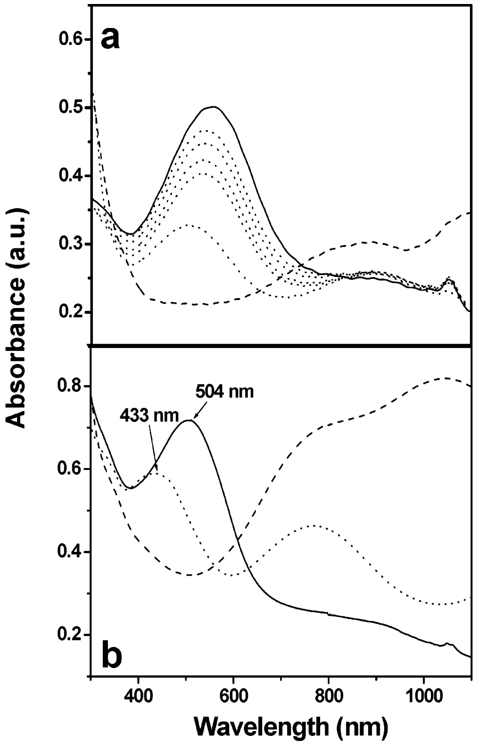


Figure 7. Evolution of the UV−vis spectra of an aqueous PEDOT-S solution upon (a) "acid doping" with a *p*-toluenesulfonic acid solution and (b) oxidative doping with ammonium persulfate solution.

Acid Doping of Polyelectrolyte Films. It was observed that aqueous solutions of neutral PEDOT-S turned blue (the color of the oxidized state) upon the addition of *p*-toluenesulfonic acid and returned to pink/purple (the neutral color) upon the addition of hydrazine. Typically the presence of a chemical oxidant or an applied potential is required to facilitate oxidation of polythiophenes and their derivatives. To investigate this "acid doping" phenomenon further, *p*-toluenesulfonic acid and a chemical oxidant, ammonium persulfate, were slowly titrated to two different aqueous solutions of PEDOT-S, and the absorption was monitored by UV−vis spectroscopy as illustrated in Figure 7. The UV−vis spectra in Figure 7a show depletion of the $\pi-\pi^*$ transition as expected for oxidation, but now resulting from the acid doping by *p*-toluenesulfonic acid. The $\pi-\pi^*$ transition gives way to an absorbance at higher wavelengths commonly associated with the presence of charge carrier states after full $\pi-\pi^*$ band depletion and is shown to be fully reversible upon the addition of hydrazine. The addition of a known chemical oxidant in Figure 7b results again in the blue coloration of the PEDOT-S solution, along with the longer wavelength transitions. A much larger charge carrier absorbance is observed upon addition of the chemical oxidant, as opposed to the acid, and suggests that the chemical oxidant results in a more highly doped polymer. Wudl et al.[9] as well as others[14] have also made similar observations during their work on sulfonated polythiophenes, but as yet, no sufficient explanation has been offered as to how the addition of acids generates charge carriers in these polymers and whether the change in optical properties is actually associated with a change in conductivity. To further investigate whether this observed acid doping is not oxidative, both perchloric acid and hydrochloric acid (a nonoxidizing acid) were added to solutions containing PEDOT-S and PEDOT-S/PAH films deposited on ITO glass. The effect of adding

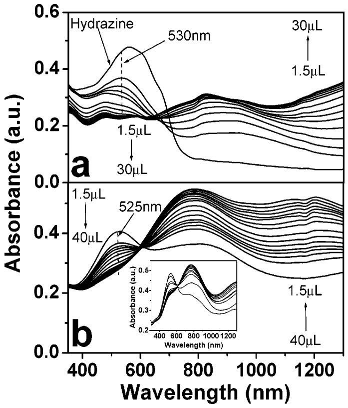


Figure 8. Acid doping of (a) PEDOT-S electrochemically deposited and (b) PEDOT-S/PAH multilayer films with perchloric acid in $LiBF_4$ (0.01 M)/acetonitrile, fully neutralized with hydrazine. Inset: acid doping of PEDOT-S/PAH in Na_2SO_4 (0.2 M)/H_2O using HCl. Reversibly neutralized with NaOH and fully neutralized with hydrazine.

a nonreducing base (sodium hydroxide) into solutions containing the oxidized films was also investigated.

The UV–vis/NIR spectra of both electrochemically deposited PEDOT-S and PEDOT-S/PAH multilayer films of 32 BL (Figure 8, a and b, respectively) were recorded in-situ, as aliquots of perchloric acid were added to the $LiBF_4$(0.1 M)/acetonitrile solution. Perchloric acid was chosen, as it was soluble in the organic electrolyte solution. The inset in Figure 8b shows the spectra of an L-B-L film in aqueous media upon the addition of hydrochloric acid. The spectra for both types of films in organic electrolyte, as seen in Figure 8a,b, show the gradual evolution of the charge carrier peaks and bleaching of the $\pi-\pi^*$ band during the acidification of the solution from 5.5×10^{-3} to 0.01 M. The same effect was also observed for PEDOT-S/PAH films in Na_2SO_4 (0.2 M)/ H_2O when the hydrochloric acid concentration was slowly increased from 7.0×10^{-3} to 0.01 M (Figure 8 inset). The optical and NIR change of the film in aqueous media was reversible upon the addition of a basic sodium hydroxide solution, although hydrazine was required to completely neutralize the polymer.

The spectra associated with acid doping of the PEDOT-S/PAH films (Figure 8b) are almost identical to those obtained during in-situ electrochemical oxidation, as seen previously in Figure 6. The PEDOT-S/PAH films are already slightly oxidized when they are deposited due to the pH-adjusted solutions from which they are deposited, which accounts for the difficulty in fully neutralizing the films electrochemically. This is likely due to trapped protons within the film. Although the electrochemically deposited PEDOT-S also undergoes a transition upon the addition of acid as seen in Figure 8a, the transitions are not as smooth in PEDOT-S as for the PEDOT-S/PAH multilayer films, and the charge carrier bands are less defined.

Conductivity Measurements and Acid Doping. To establish whether acid doping of PEDOT-S/PAH is accompanied by an increase in the conductivity, 150 nm thick multilayer films were deposited onto glass slides to enable four-point probe conductivity measurements to be carried out. The conductivity was measured on films as deposited and then after submersion into a solution containing NaOH in Na_2SO_4 (0.2 M)/H_2O and HCl in Na_2SO_4 (0.2 M)/H_2O consecutively. The average conductivity value from four films was 2.5×10^{-4} S/cm for as-deposited films, 7.2×10^{-5} S/cm for sodium hydroxide-treated films, and 2×10^{-4} S/cm after films were treated with hydrochloric acid. Although these values are low, the conductivity in all cases decreased after the film is submerged into basic solution and then increased again upon submersion into the acidic solution. The films were washed and dried thoroughly before each conductivity measurement was taken. In comparison, the conductivity of PEDOT/PSS (Bayer) films is similar at 2.9×10^{-4} S/cm. It is already known that for applications such as the hole injection layers in LEDs a high level of conductivity is not required (or even desired) to achieve efficient hole transport. From these results it has been shown that "acid doping" and the resultant color changes of the films are accompanied by a change in conductivity.

Electrochromic Properties of PEDOT-S. It was originally thought that directly attaching the dopant anion to the thiophene backbone in sulfonate functionalized self-doped polymers would increase the doping level and hence increase the electrochromic contrast between the oxidized and neutral states of the polymer. For PEDOT-S, the change in transmisivity and the color contrast were not as large as we have observed organic soluble 3,4-propylenedioxythiophene polymers which are deposited by spray coating.[30] At the same time, the PEDOT-S/PAH exhibits surprisingly fast switching and high coloration efficiencies and suggests that only a small amount of charge is required to switch the polymer between the neutral and oxidized states. Despite the high coloration efficiency of PEDOT-S/PAH, in order for the polymer to be fully effective in electrochromic display devices, the optical contrast will of these polymer films will need to be enhanced. At the same time they may find utility in other coloration-type devices such as sensors and indicators due to their chemical (acid/base and redox) sensitivity.

PEDOT-S/PAH Multilayer Films in Near-IR OLEDs. The homogeneous film quality and good charge transport properties displayed by PEDOT-S/PAH seem well-suited to applications such as the hole injection layer in OLEDS. Previously, layer-by-layer deposited films have been employed as the light-emitting layer in OLEDs as it has been shown to improve charge transport within the films.[22] PEDOT/PSS is well-known as a good hole injection layer in OLEDs; however, the use of LBL films as hole injection layers has predominantly focused on multilayers incorporating PPV [poly(phenylenevinylene)[31] or other semiconducting polymers such as PANI (polyanilline).[32] Existing technology within our group allowed the construction of near-IR electroluminescent devices,[5] based upon a 10 mol % PPP-OR11: $Yb(DNM)_3$ phen complex, with PEDOT-S/PAH and PEDOT/PSS as the holing injecting layers for comparison. The current density and irradiance of the resulting near-IR emission at 977 nm are seen in Figure 9 as a function of applied voltage. It is evident from this study that the properties of PEDOT-S/PAH as a charge transport layer are comparable to PEDOT/PSS, and this method may prove useful in situations where irregularly shaped surfaces not conveniently coated by spin-coating are desired as light-emitting surfaces.

Conclusions and Perspective

We have compared the chemical and electrochemical synthesis of PEDOT-S as well as the deposition of PEDOT-S in layer-by-layer films. Both electrochemically deposited PEDOT-S and PEDOT-S/PAH were charac-

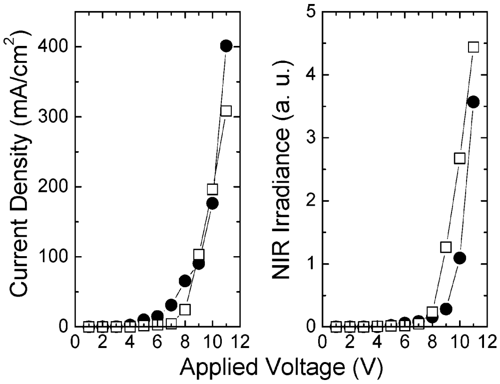


Figure 9. NIR (977 nm) EL characteristics from ITO/HTL/Yb(DNM)$_3$phen+PPP-OR11/Ca/Al devices as a function of applied potential. Solid circles: ITO/PEDOT-S/10 mol % Yb-(DNM)$_3$phen + PPP-OR11/Ca/Al device; open squares: ITO/PEDOT-PSS/10 mol % Yb(DNM)$_3$phen + PPP-OR11/Ca/Al device.

terized by electrochemical and spectroscopic methods to show that the switching of the PEDOT-S/PAH films in both aqueous and organic media is more efficient than electrochemically deposited PEDOT-S films in which ion mobility appears to be poor. Acid doping of PEDOT-S is illustrated, and it was found that the conductivity of PEDOT-S/PAH is observed to increase upon exposure to acid and decrease upon exposure to base. This change in conductivity is accompanied respectfully by a notable color change. While it was found that the change in color is rapid when electrochemically initiated, the contrast is lower than many electrochromic polymers. Alternate uses for PEDOT-S/PAH may be found in sensors and indicators and as a more soluble and proccessable option than PEDOT/PSS as the hole injection layer in OLEDs. It was found that these films are comparable in performance to PEDOT/PSS as a hole injection material. Optimization of the use of PEDOTS/PAH in OLEDs may provide a viable alternative to PEDOT/PSS in the future.

Acknowledgment. Partial support of this work from the Department of Energy, Basic Energy Sciences Program (DE-FG-02-96ER14617), is gratefully appreciated.

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MA047396+