

Polymer Composite with Three Electrochromic States

Jiangfeng Fei,[†] Keng Guan Lim,[†] and G. Tayhas R. Palmore^{*,†,‡}

Division of Engineering and Division of Biology and Medicine, Brown University, Providence, Rhode Island 02912

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The electrochromic properties of an electrodeposited polymer composite consisting of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(3-methyl-2-[[3-(4-vinyl-benzyl)-3H-benzothiazol-2-ylidene]-hydrazono]-2,3-dihydro-benzothiazole-6-sulfonic) acid (polyABTS) are reported. Films of this polymer composite exhibit three electrochromic states in the visible region upon application of potentials at -800 mV, 0 V, and $+800$ mV versus Ag/AgCl, confirming that both polymers contribute to electrochromic switching. These films exhibit ultracontrasts between the bleached state at 0 V and the blue state at -800 mV ($\Delta T \% = 33.6\%$ at 615 nm) and the green state at $+800$ mV ($\Delta T \% = 46.3\%$ at 393 nm). The efficiency of cathodic coloration and bleaching of this material at 615 nm is 322.1 and 396.4 $\text{cm}^2 \text{C}^{-1}$, respectively, whereas the efficiency of anodic coloration and bleaching at 393 nm is 189.9 and 192.4 $\text{cm}^2 \text{C}^{-1}$, respectively. In comparison to previously reported films of polypyrrole (pPy) doped with the ABTS monomer (pPy[ABTS]), thick films of PEDOT[polyABTS] exhibit an increased stability to potential cycling both because PEDOT is more resistant to overoxidation than pPy and because polyABTS is a nonleachable dopant. Reversible redox behavior, anodic and cathodic coloration, fast response times, resistance to overoxidation, ease of fabrication, and low cost make this material competitive for electrochromic applications.

Introduction

Since their discovery,^{1–3} conductive polymers have been studied extensively because of their fascinating physics and broad potential in technological applications. Conductive polymers can be synthesized via chemical or electrochemical oxidation,^{4–6} producing a polycationic material that requires charge-compensating dopants. A variety of anionic dopants have been used, including Cl^- ,⁷ ClO_4^- ,⁸ BF_4^- ,⁹ *p*-toluenesulfonate,¹⁰ dodecylbenzenesulfonate (DBS),¹¹ and polystyrene sulfonate (pSS),¹² all of which function to balance the cationic charge of the conductive polymer.

More recently, other dopants have been used, which in addition to balancing charge, possess a distinct charac-

teristic that imparts a new property or function to the conductive polymer (typically pPy, polythiophene, or PEDOT). For example, proteins and peptide dopants impart bioactivity,¹³ whereas carbon nanotubes enhance mechanical strength.¹⁴ Redox-active dopants improve charge transfer between electrodes of biofuel cells and biosensors to the active site of enzymes embedded in the conductive polymer,¹⁵ improve the energy density of batteries made from conductive polymers,¹⁶ yield a light-harvesting material,¹⁷ and add new colored states in electrochromic films.¹⁸ Examples of redox-active dopants include indigo carmine (IC),^{18,19} 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS),^{16,18} ferrocyanide $\{\text{Fe}(\text{CN})_6^{4-}\}$,^{20,21} metallophthalocyanines (MePc),^{22–25}

* Corresponding author. E-mail: Tayhas_Palmore@brown.edu.

[†] Division of Engineering.

[‡] Division of Biology and Medicine.

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metalloporphyrins (MePp),^{18,26,27} hydroquinone sulfonate (HQS),²⁸ and tris(2,2'-bipyridine)ruthenium (II) (Ru(bpy)₃²⁺).¹⁷

Synthetic approaches to modifying the electrochromic properties of conducting polymers include the use of derivatives of 3,4-ethylenedioxythiophene (EDOT)²⁹ or pyrrole monomers^{30–32} or the copolymerization of EDOT with carbazole,³³ pyridine,³⁴ or pyridopyrazine.³⁵ Recently, a multielectrochromic material was prepared from a derivative of EDOT bearing a viologen-containing substituent.³⁶ An excellent reference detailing the theory, synthesis, properties, and characterization of electrochromism in conducting polymers has been published recently.³⁷

In 1998, Girotto and De Paoli demonstrated that polypyrrole (pPy), doped with both dodecylsulfate (DS) and IC (a water-soluble dye), yielded a material (pPy[DS/IC]) with enhanced electrochromic properties (i.e., contrast, optical memory, and response times) as compared to films of polypyrrole doped with only DS (i.e., pPy[DS]).¹⁹ More recently, Song et al. elaborated on the work of Girotto and De Paoli and showed that pPy doped with 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS), a monomeric electrochromogen, yielded a material with an additional electrochromic state for a total of three colored states (i.e., yellow, gray, and green).¹⁸ The significance of both of these studies is that they demonstrated a simple, nonsynthetic approach to improving the electrochromic properties of a known electrochromogen (i.e., pPy).

Despite this simple approach to improve or change the electrochromic properties of these materials, several issues remain. First, the stability of electrochromic enhancement of pPy doped with monomeric dopants is limited due to the discharge of dopants with potential cycling. Second, the stability of an anodic electrochromic state in films made with pPy is limited because of the oxidative susceptibility of pPy to potentials more positive than 650 mV versus Ag/AgCl.³⁸ Third, the low contrast in films made with pPy reduces its

value as an electrochromic material in many applications such as smart windows and display technologies.¹⁸ All three of these issues can be addressed by using an electrochromic dopant that is polymeric and a conductive polymer that is both stable to oxidation and more transparent than polypyrrole.

Herein, we report the electrochromic properties of a polymer composite (PEDOT[polyABTS]) consisting of poly(3,4-ethylenedioxythiophene) (PEDOT)³⁹ doped with a polymeric version of ABTS (polyABTS) recently synthesized in our laboratory.⁴⁰ Using a polymeric dopant is shown to eliminate all instability in these films due to the loss of dopant. Furthermore, films of PEDOT[polyABTS] exhibit three electrochromic states (blue, gray, and green) and are stable to potentials as high as 1.05 V versus Ag/AgCl, whereas films of pPy[ABTS] are stable only to 650 mV versus Ag/AgCl. In terms of contrast, the anodic coloration of PEDOT[polyABTS] increased several times over that of pPy[ABTS], whereas the cathodic coloration of PEDOT[polyABTS] is similar to that reported for PEDOT doped with pSS. Finally, the stability, efficiency of coloration and bleaching, optical memory, and color difference of PEDOT[polyABTS] were found to be higher than those of the previously reported pPy[ABTS].

Results and Discussion

Conductive polymers, such as PEDOT and pPy, can be electropolymerized using a variety of electrochemical methods including chronopotentiometry, chronoamperometry, and cyclic voltammetry (CV). For electrochromic applications, the most stable films of conductive polymers are prepared via CV.¹⁸ PEDOT and pPy are cationic in their conductive states, where one cationic charge is present for every three subunits of EDOT and every three to five subunits of pyrrole.^{5,6,41–45} Electrooxidation of EDOT or pyrrole in the presence of polyanionic polyABTS or pSS results in an electrodeposited film consisting of the respective conductive polymer (PEDOT or pPy) doped with polyABTS or pSS (Figure 1).

The range of potentials swept during the electrooxidation of EDOT or pPy can be used to control the thickness of the electrodeposited film. For example, thin films (~180 nm) of PEDOT[polyABTS] can be prepared by sweeping the potential between 0 and 1.0 V at a scan rate of 100 mV/s, whereas slightly thicker films (~230 nm) of PEDOT[polyABTS] can be prepared by narrowing the potential range to between 0.4 and 1.0 V.⁴⁶ Narrowing the potential range to

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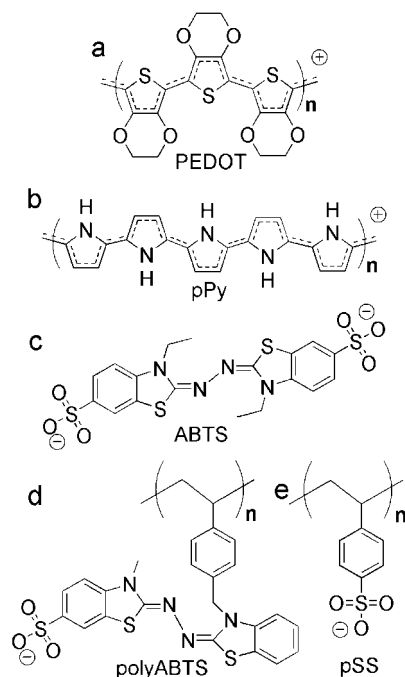


Figure 1. Molecular structures of (a) polycationic PEDOT, (b) polycationic pPy, (c) dianionic ABTS, (d) polyanionic polyABTS, and (e) polyanionic pSS.

less negative values decreases the amount of time that the oxidized oligomer has to diffuse away from the surface of the electrode and consequently increases the amount of oxidized oligomer that adds to the growing polymer chain.

Monomeric versus Polymeric ABTS as Anionic Dopants to Conductive Polymers. Monomeric ABTS is a dianion and therefore can function as a redox-active dopant in polycationic conductive polymers such as PEDOT or pPy.^{16,18} With repeated potential cycling, however, monomeric dopants such as ABTS will diffuse out of the conductive polymer matrix, resulting in a film with a reduced redox activity and electrochromogenicity. Shown in Figure 2a is the time-dependent absorbance data of a solution (sodium phosphate, pH 7) exposed to an electrode coated with a film of PEDOT[ABTS] or pPy[ABTS]. The absorbance of both solutions continuously changed over the 12 h experiment, indicating a loss of ABTS from the conductive polymer films. On the basis of the extinction coefficient of ABTS ($3.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),⁴⁷ films of pPy[ABTS] lose ABTS at a rate of 1.35 nmol/h over a 12 h period. To put this rate of discharge into context, the concentration of monomeric ABTS in an electrodeposited film of pPy[ABTS] prepared under identical conditions was found to be 2.9 M.¹⁶ For a disk-shaped film that measures 2 mm in diameter and 4 μm thick, the total amount of ABTS in the film was 36.4 nmol. As such, only 24 h would be needed to discharge most of the ABTS from the film, rendering the material nonelectrochromic at positive potentials.

In comparison to films of pPy[ABTS], films of PEDOT[ABTS] lose ABTS at a slightly lower rate (0.88 nmol/h) over the same period of time. This difference in rate of discharge may reflect a difference in the density of packing

of the two polymer composites.^{21,48} Recall that the ratio of cationic sites per monomer subunit is 1:3–5 in pPy and 1:3 in PEDOT. Consequently, cross-linking of polycationic strands by dianionic ABTS may occur more frequently in PEDOT than in pPy, resulting in a denser, less porous film that could slow the rate of discharge of ABTS. Nevertheless, the loss of ABTS from either of the films yields a material with an unstable electrochromic state.

To prevent the loss of dopant from a conductive polymer and the consequential impact on the electrochromic properties of the film, larger dopants were used. For example, pSS has been used as a nonleachable dopant in pPy and PEDOT.^{49,50} For this study, a polymerizable derivative of ABTS was synthesized,⁴⁰ and the resulting redox-active polymer (poly-ABTS) was used as the polyanionic dopant in films of pPy and PEDOT. Illustrated in Figure 2b is the one-electron redox reaction between oxidized and reduced forms of polyABTS. The absorption spectrum of polyABTS in its reduced state has a strong absorbance at 340 nm. Upon oxidation, each ABTS subunit of polyABTS loses one electron to form the green radical (ABTS[•]), which absorbs at 393, 650, and 740 nm. Note that the absorption maxima in monomeric ABTS[•] (415, 645, and 730 nm) are slightly different from those of polyABTS.^{18,47} The redox potentials of both the polymerizable monomer of ABTS (sABTS, s = styrl) and its corresponding polymer (polyABTS) are identical to commercial ABTS, which is 510 mV versus Ag/AgCl in aqueous electrolytes.⁴⁰ Returning to the data shown in Figure 2a, it is immediately apparent that the absorbance of a solution exposed to an electrode coated with films of PEDOT[poly-ABTS], pPy[polyABTS], or polyABTS remains constant over the time frame of the experiment (i.e., zero absorbance at 340 nm), indicating that polyABTS is not released by the films into solution.

Electrochemical Evaluation of Films of polyABTS and PEDOT[polyABTS]. Shown in Figure 3 are the cyclic voltammograms of an ITO/glass electrode coated with either a physisorbed film of polyABTS (~70 nmol) or a film of electrodeposited PEDOT[polyABTS] (both thick and thin films with ~60 nmol of polyABTS). The CV image of polyABTS reveals a redox couple centered at 510 mV with oxidative and reductive peaks at 660 and 330 mV, respectively. Included in Figure 3 are the CV images of thick and thin films of PEDOT[polyABTS]. Two features have changed in the CV image of polyABTS as a consequence of PEDOT being present. First, the amount of faradaic charge has increased despite similar concentrations of polyABTS in all films. This change indicates that PEDOT facilitates electron transport to redox-active groups further away from the surface of the electrode. Second, the oxidative and reductive peaks are centered at a slightly more positive potential (i.e., 540 mV) with a peak-to-peak separation of 640 mV. The increase in the separation between anodic and cathodic peaks indicates that electron self-exchange between ABTS neighbors is slower in the presence of conductive PEDOT. This

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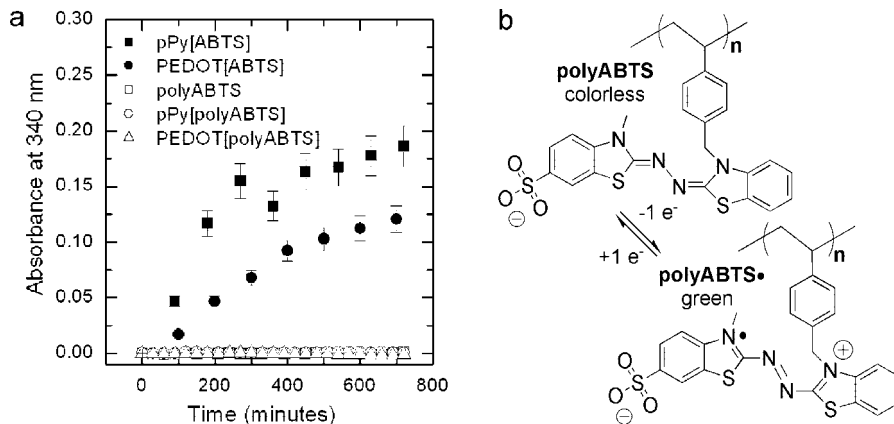


Figure 2. (a) Absorbance of solutions (sodium phosphate, pH 7) exposed to electrodes coated with different polymer films as a function of time. (b) Molecular structures of reduced (polyABTS) and oxidized (polyABTS^{•+}) forms of polyABTS.

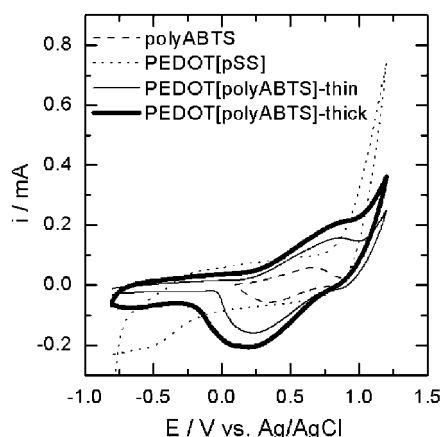


Figure 3. CV images of an ITO/glass electrode coated with either a physisorbed film of polyABTS or electrodeposited films of PEDOT[polyABTS] (thick and thin). The CV image of an ITO/glass electrode coated with an electrodeposited film of PEDOT[pSS] is included for comparison. All CV images were measured in an aqueous electrolyte (200 mM KCl, pH 5.5) at a scan rate of 10 mV s⁻¹.

change may stem from structural changes (i.e., mechanical stiffening and/or reduced permeability) caused by the addition of PEDOT. Mechanical stiffening of the film would reduce the frequency of collision between redox-active sites, whereas reduced permeability would impede the mobility of charge-compensating counterions.^{51,52} Included for comparison is a CV image of an electrode coated with PEDOT[pSS], which is dominated by nonfaradaic charging at potentials near to or more negative than $E_{1/2}$ of polyABTS. In addition, a strong oxidative peak appears at 1 V that is suppressed in the CV images of electrodes coated with polyABTS or PEDOT[polyABTS].

Electrochromic Behavior of Films of PEDOT[poly-ABTS]. The conductive polymer, PEDOT, has been studied extensively because of its high conductivity and stability against oxidizing potentials.^{4,53–55} Electrochromic films can be produced by doping PEDOT with a variety of dopants

including Prussian blue,⁵⁶ 1-butyl-3-methylimidazolium tetrafluoroborate,^{57,58} tetrabutylammonium hexafluorophosphate,⁵⁹ sodium dodecyl sulfate (SDS),⁶⁰ LiClO₄,^{61,62} pSS,^{50,63} and hydroxypropyl cellulose.⁶⁴ Of these films, PEDOT[pSS] has received the most attention because of its good conductivity (10 S cm⁻¹), stability at oxidizing potentials, and transparency. Films of PEDOT[pSS] have been demonstrated to function as a proton exchange membrane,⁶⁵ a write-once read-many (WORM) memory device,⁶⁶ and a field-effect transistor (FET).⁶⁷

As previously discussed, a thick film of PEDOT[poly-ABTS] (230 nm) is produced when the potential is swept between 0.4 and 1.0 V, resulting in more PEDOT being electrodeposited. Expanding the potential range to 0.0 to 1.0 V results in less PEDOT being electrodeposited and a corresponding film that is 50 nm thinner (180 nm). The ratio of PEDOT to polyABTS in a film can be determined from their respective absorption bands at 615 and 390 nm in transmission spectra after subtracting a background absorbance due to the ITO-coated glass and electrolyte. On the basis of the transmission spectra shown in Figure 4, the amount of polyABTS electrodeposited with PEDOT is nearly the same regardless of the thickness of the film. Moreover, 3 times as much PEDOT is present in the thicker film of PEDOT[polyABTS] than the thinner film. Recall that PEDOT is cationic in its conductive state, where one cationic

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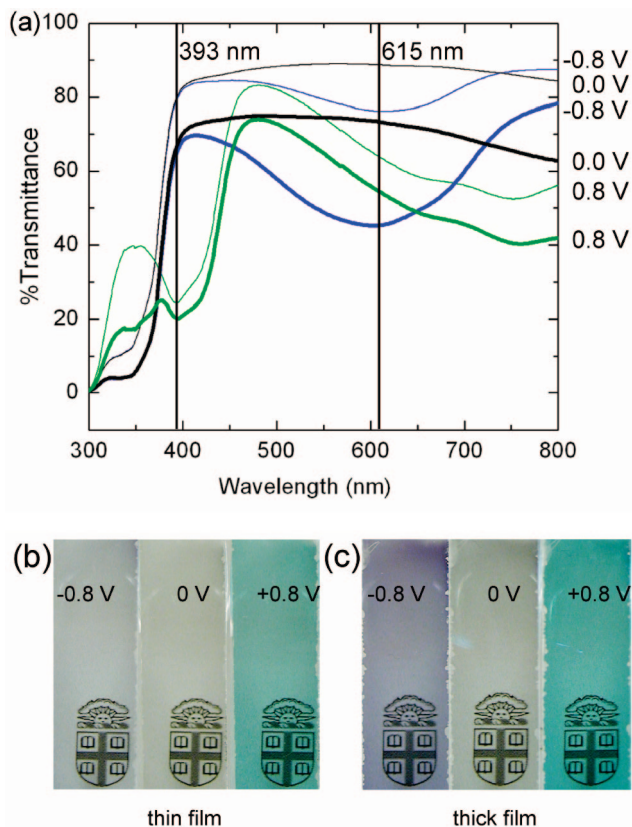


Figure 4. (a) Transmission spectra of ITO/glass coated with thin (—) and thick (---) films of PEDOT[polyABTS] when the films were poised at cathodic (−800 mV, blue lines), bleaching (0 V, black lines), and anodic potentials (800 mV, green lines). Photographs of the electrodes at different potentials: (b) thinly coated electrode and (c) thickly coated electrode.

charge is present for every three subunits of EDOT. Thus, based on the lower ratio of PEDOT to polyABTS in a thin film of PEDOT[polyABTS] as compared to a thick film, a mobile cation from the electrolyte (i.e., K^+) must also be present in the thick film to maintain the overall charge balance.

Spectroelectrochemistry of PEDOT[polyABTS]. The transmission spectra shown in Figure 4 reveal the absorption bands corresponding to the three electrochromic states of thick and thin films of PEDOT[polyABTS] electrodeposited onto ITO-coated glass. The cathodic coloration (blue color at −800 mV) is attributed to the reduction of PEDOT itself. When the working electrode is poised at 0 V, the color bleaches to give a transparent gray state. Anodic coloration (green color at 800 mV) is attributed to the oxidation of polyABTS to its radical form.

The transparency of a film of PEDOT[polyABTS] at 0 V is similar to that of the previously reported film of pPy-[ABTS].¹⁸ In the visible region of the spectrum (400–800 nm), the transmittance of a film of PEDOT[polyABTS] is thickness dependent: the transmittance of thin films is greater than 83%, whereas for thick films, the transmittance is between 63 and 75%. When the electrode was poised at 800 mV, the spectra of both thick and thin films of PEDOT[polyABTS] contained signature peaks corresponding to polyABTS* (393, 650, and 740 nm). The peak corresponding to reduced PEDOT appears at 615 nm upon reversal of the

potential to −800 mV. The values for various electrochromic parameters of films of PEDOT[polyABTS] are summarized in Table 1. Included for comparison are the values for a film of PEDOT[pSS] prepared in our laboratory and values for a film of pPy[ABTS] reported in the literature.¹⁸ In general, the electrochromic properties of films of PEDOT[polyABTS] and PEDOT[pSS] are similar at cathodic potentials.

Percent Transmittance. The percent transmittance ($\Delta T\%$, also known as “contrast”) of both thick and thin films of PEDOT[polyABTS] was traced as a function of applied potential at 393 and 615 nm. A thin film of PEDOT[polyABTS] has a higher $\Delta T\%$ (55%) at 393 nm but a lower $\Delta T\%$ (12.4%) at 615 nm as compared to that of a thick film (46.3% at 393 nm and 33.6% at 615 nm) as shown in Figure 4. These differences are the result of more PEDOT present in the thick film, which gives a darker background color at 0 V. Consequently, a thin film of PEDOT[polyABTS] produces a higher contrast of green, whereas a thick film of PEDOT[polyABTS] produces a higher contrast of blue. It should be noted that films consisting of both poly(hexyl viologen) (PXV) and PEDOT[pSS] that were prepared via a layer-by-layer method exhibited the highest value for contrast (82.1% at 525 nm) reported in the literature.⁶⁸

Response Times and Efficiency of Coloration and Bleaching. Cathodic coloration and bleaching correspond to the reduction and oxidation of PEDOT, respectively, in PEDOT[polyABTS] and depend on electron transfer between electrode and PEDOT and rapid electron transport along conductive PEDOT chains. Thus, the response times (measured at the wavelength specified in Table 1 by UV-vis spectroscopy) for cathodic coloration (1.2 s) and bleaching (1.2 s) in thick films of PEDOT[polyABTS] are fast and similar to those observed in films of PEDOT[pSS]. Anodic coloration and bleaching correspond to the oxidation and reduction of ABTS, respectively, in PEDOT[polyABTS]. The response times for anodic coloration (15–16 s) and bleaching (11 s) are similar in both thick and thin films of PEDOT[polyABTS] but slower than the cathodic processes because oxidation and reduction of ABTS in PEDOT[polyABTS] depend partly on a self-exchange mechanism that depends on collisions between electron carriers and therefore is slow as compared to electron transport in conductive polymers.⁶⁹

The efficiency of coloration and bleaching, η ($\text{cm}^2 \text{C}^{-1}$), at a given wavelength is given by

$$\eta = \frac{\Delta \text{OD}}{Q_d} = \frac{\log[T_b/T_c]}{Q_d} \quad (1)$$

where ΔOD is the change in optical density, Q_d is injected or ejected electronic charge (C cm^{-2}), and T_b and T_c are the transmittance values (intensity of absorbance) for the bleached and colored states, respectively.⁷⁰ The values for T_b and T_c that correspond to bleaching and anodic coloration of films of PEDOT[polyABTS] were taken from Figure 4 at 393 nm, whereas the values for T_b and T_c that correspond to bleaching

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Table 1. Electrochromic Parameters of Films of PEDOT[polyABTS], PEDOT[pSS], and pPy[ABTS]

film	ΔT %	coloration response time (s)	bleaching response time (s)	coloration efficiency ($\text{cm}^2 \text{C}^{-1}$)	bleaching efficiency ($\text{cm}^2 \text{C}^{-1}$)	stability (% change)/x cycles	color difference (ΔE) ^a
PEDOT[polyABTS]-thin (anodic coloration at 393 nm)	55.0	16.1	11.0	270.3	274.9	50%/1500	22.0
PEDOT[polyABTS]-thick (anodic coloration at 393 nm)	46.3	15.0	10.8	189.9	192.4	9%/3000	18.0
pPy[ABTS]-thin (anodic coloration at 413 nm)	4.5	4.7	0.5	33.0	77.0	50%/500	3.8
pPy[ABTS]-thick (anodic coloration at 413 nm)	23.0	12.0	1.2	82.0	150.0	6%/1500	11.0
PEDOT[polyABTS]-thick (cathodic coloration at 615 nm)	33.6	1.2	1.2	322.1	396.4	7%/3000	16.0
PEDOT[pSS] (cathodic coloration at 615 nm)	36.8	2.4	2.4	297.1	396.1	6%/3000	46.7

^a Cathodic coloration was achieved by application of a potential step from 0 mV (colorless) to -800 mV (blue); bleaching was achieved by application of a potential step from -800 to 0 mV or 800 to 200 mV; and anodic coloration was achieved by application of a potential step from 200 mV (colorless) to 800 mV (green) except in the case of pPy[ABTS], where the potential step was from 0 to 600 mV. All potentials are reported vs Ag/AgCl.

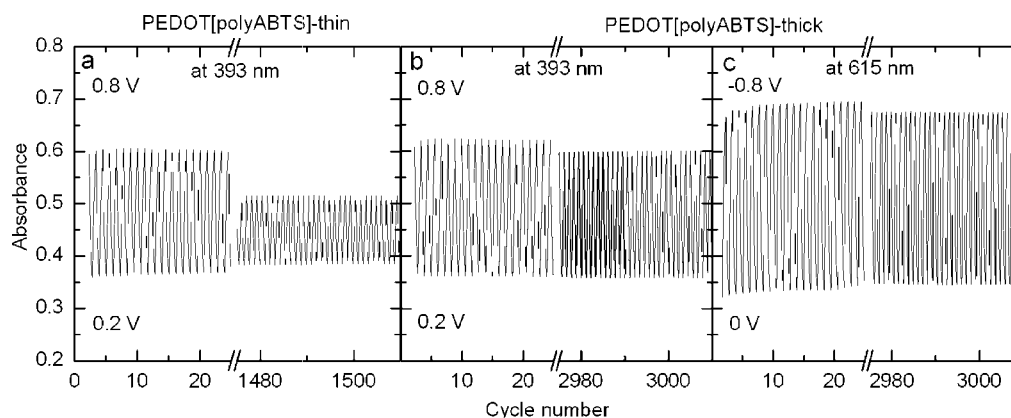


Figure 5. Potential cycling of PEDOT[polyABTS] and corresponding change in percent transmittance (ΔT %) at 393 nm (anodic coloration) or 615 nm (cathodic coloration): (a) thin and (b) thick films cycled between 0.2 V (bleaching) and 0.8 V (anodic coloration) and (c) thick film cycled between 0.0 V (bleaching) and -0.8 V (cathodic coloration).

and cathodic coloration were taken from Figure 4 at 615 nm. A notable difference in the efficiency of anodic coloration and bleaching is observed in films of PEDOT[polyABTS], where thin films are more efficient (i.e., $270.3 \text{ cm}^2 \text{C}^{-1}$ for coloration and $274.9 \text{ cm}^2 \text{C}^{-1}$ for bleaching) than thick films (i.e., $189.9 \text{ cm}^2 \text{C}^{-1}$ for coloration and $192.4 \text{ cm}^2 \text{C}^{-1}$ for bleaching). This difference is observed only at positive potentials and indicates that a portion of the injected and ejected charge is used to charge and discharge the additional PEDOT in a thick film instead of producing a color change by oxidizing ABTS subunits in polyABTS.

Film Stability Against Potential Cycling. The stability of films of PEDOT[polyABTS] was evaluated by monitoring ΔT % while cycling the potential. Shown in Figure 5a,b are anodic cycling data (between 0.2 and 0.8 V) from thin and thick films of PEDOT[polyABTS], respectively. After only 1500 cycles, ΔT % of the thin film decreases to half of its original value. In contrast, ΔT % of the thick film decreases by less than 9% after 3000 cycles. Shown in Figure 5c are cathodic cycling data (0 and -0.8 V) from a thick film of PEDOT[polyABTS], which reveals that ΔT % decreased by less than 7% after 3000 cycles.

Electrochromism in films of PEDOT has been observed to degrade with potential cycling, the cause of which has been attributed to thermal,⁷¹ photo,⁷² and pH effects;⁷³ desorption of the films;⁶⁸ and even acid etching of the ITO

substrate by pSS.⁷⁴ To rule out any issues with the ITO substrate (i.e., acid etching by polyABTS), both thick and thin films of PEDOT[polyABTS] were electrodeposited onto a GC electrode using the same procedures described for an ITO electrode and subsequently subjected to potential cycling identical to that described previously.

Shown in Figure 6 are CV images of both thick and thin films of PEDOT[polyABTS] before and after 3000 cycles between 200 and 800 mV. Recall that a thin film of PEDOT[polyABTS] contains a lower concentration of PEDOT than a thick film on the basis of their corresponding transmission spectra (cf., Figure 4), which is confirmed by the relative size of the peaks at 1 V (corresponding to the oxidation of PEDOT) in both CV images shown in Figure 6. The CV images of both thick and thin films of PEDOT[polyABTS] on GC electrodes decrease in area after 3000 cycles, with the most significant decrease observed in the CV of the thin film. Because the electrode material is GC instead of ITO, the decrease in current in the CV is not due to acidic etching of the underlying substrate by polyABTS.

The most significant change in the CV images is at 1 V, where overoxidation of PEDOT is known to occur.⁷⁵ Similar behavior is observed in films of PEDOT[pSS] prepared in our laboratory. A decrease in the current observed at this potential indicates that less PEDOT is available to be

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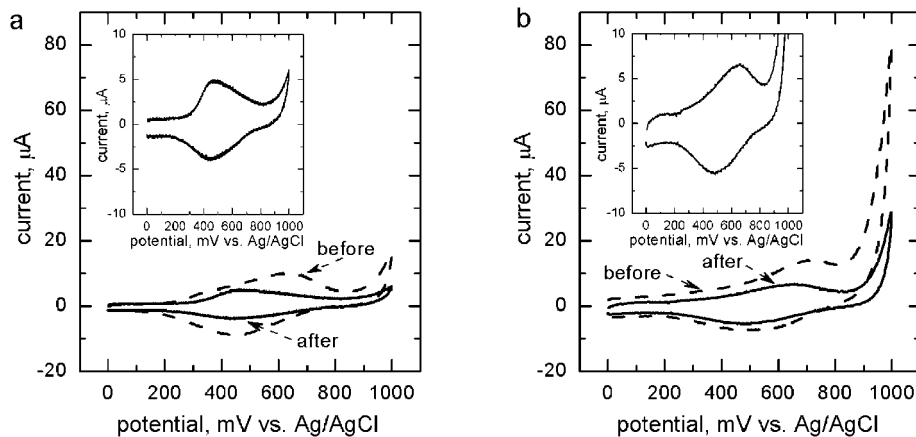


Figure 6. CV images of (a) thin and (b) thick films of PEDOT[polyABTS] electrodeposited onto a GC electrode before (dashed line) and after (solid line) cycling the potential 3000 times. The insets are enlargements of the last CV image taken after potential cycling.

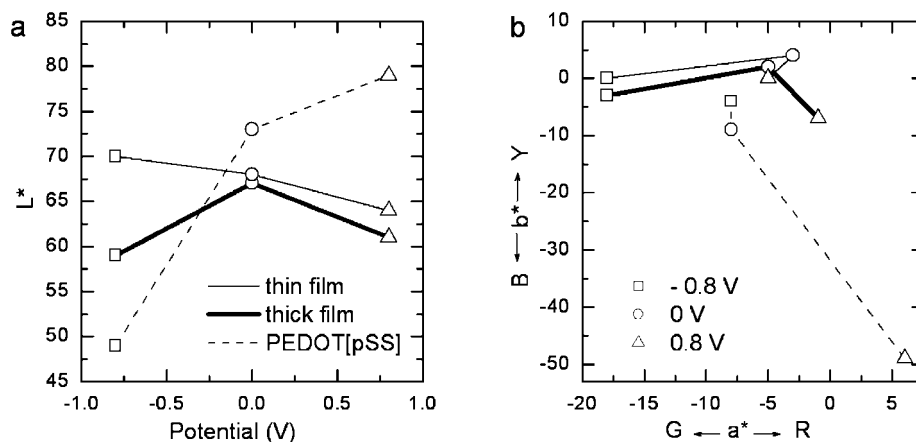


Figure 7. CIE $L^*a^*b^*$ coordinates of color of PEDOT[polyABTS] films.

oxidized with each cycle. Overoxidized PEDOT is nonconductive,⁷⁵ and therefore, electron transport between polyABTS and the electrode becomes more difficult as the concentration of nonconductive PEDOT increases in the film. Close inspection of the final CV image (shown enlarged in the inset) of each film reveals peaks centered at 450 mV, which correspond to the reversible oxidation and reduction of polyABTS near the surface of the electrode. On the basis of the area of the CV image, the amount of electrochemically accessible polyABTS in the thin film is 50% of the original amount of polyABTS (~ 2 nmol) electrodeposited with PEDOT. Similar changes were observed in the thick film of PEDOT[polyABTS]. The peak-to-peak separation is 0 V in the CV image of the thin film and 190 mV in the CV image of the thick film.

Optical Memory. The optical memories of both thick and thin films of PEDOT[polyABTS] were determined by monitoring the absorption band at 393 nm after the applied potential (0.8 V) was removed. Over a 30 min period, the open circuit voltage of thick and thin films decreased to 0.62 and 0.65 V, respectively. Transmittance at 393 nm for the thick film decreased by 5.5%, corresponding to a 14% variation with respect to total chromic change. Similarly, transmittance at 393 nm for the thin film decreased by 2.2% corresponding to a 4.5% variation with respect to the total chromic change. Thus, the optical memory of PEDOT[poly-

ABTS] is similar to that of pPy[ABTS] and many other electrochromic materials, which requires a periodic application of a small amount of charge to maintain maximum coloration.

Colorimetric Analysis. CIE $L^*a^*b^*$ (CIELAB) is the most complete color model used to describe all the colors visible to the human eye.⁷⁶ The three parameters in the model represent the lightness of the color (L^* , where 0 is black and 100 is white), its position between magenta and green (a^* , where negative values tend toward green and positive values tend toward magenta), and its position between yellow and blue (b^* , where negative values tend toward blue and positive values tend toward yellow). From the transmission spectra, CIE color coordinates and differences were calculated for each potential and are shown in Figure 7.^{70,77} On the basis of the coordinates shown in Figure 7a, the components of green in both films become stronger at the onset of anodic coloration, while the blue color of both films, especially for the thick film, becomes stronger with the onset of cathodic coloration. As shown in Figure 7b, both thick and thin films of PEDOT[polyABTS] have a fairly bright

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color ($L^* = 60\text{--}70$). As compared to electrodeposited films of PEDOT[pSS], the value for L^* is lower at anodic potentials but higher at cathodic potentials. The color difference (ΔE^*) of both thin and thick films is given by

$$\Delta E^* = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (2)$$

where ΔL , Δa , and Δb represent changes in the previously defined parameters (L , a , b) as the film changes from a colored to a bleached state. The calculated anodic color differences of thick and thin films of PEDOT[polyABTS] are 18 and 22, respectively. Films of PEDOT[pSS] do not have a corresponding anodic chromic state for comparison. The calculated cathodic color difference of a thick film of PEDOT[polyABTS] is 16, which is less than half the value reported for films of PEDOT[pSS] (i.e., 46.7). Consequently, films of PEDOT[pSS] are more blue (cf. Figure 7b, $y = -49$) than films of PEDOT[polyABTS].

Efficiency of Coloration and Response Times. The efficiency of coloration and bleaching of a thick film of PEDOT[polyABTS] is at the same level of electrodeposited films of PEDOT[pSS] and previously published values of chemically synthesized films of PEDOT[pSS] that were spin-coated onto an electrode surface.⁷⁸ A diffraction grating (300 and 600 lines/mm) fabricated from PEDOT[pSS] was reported that exhibits a significantly higher value ($371 \text{ cm}^2 \text{ C}^{-1}$) than a smooth, nondiffractive film ($174 \text{ cm}^2 \text{ C}^{-1}$).⁷⁸ The response time of a thick film of PEDOT[polyABTS] (1.2/1.2 s) also is in the same range as that reported for films of PEDOT[pSS] prepared via the layer-by-layer method. For example, the response times for coloration and bleaching of 20 layers of PXV/PEDOT[pSS] are 1.2 and 1.3 s, respectively. For 20 layers of poly(ethylene imine)/PEDOT[pSS], the corresponding response times are 1.22 and 0.37 s.^{68,79}

Conclusion

A polymer composite exhibiting three electrochromic states was prepared by doping PEDOT with the redox-active polymer, polyABTS. As compared to polypyrrole doped with ABTS monomers (pPy[ABTS]),¹⁸ both thick and thin films of PEDOT[polyABTS] perform better in all respects (ΔT %, color difference, efficiency, stability, and optical memory) with the exception of response times for coloration and bleaching when an anodic potential is applied. This improved performance stems from the high potentials required to overoxidize PEDOT, its high contrast, and a nondiffusing redox-active dopant.

When the properties of films of PEDOT[polyABTS] with different thicknesses are compared, thin films perform better than thick films in all respects (ΔT %, color difference, efficiency, optical memory, and response time of coloration/bleaching) except stability. This improved performance is due to a lower ratio of PEDOT to polyABTS in thin films of PEDOT[polyABTS] as compared to thick films. As compared to the properties of films of PEDOT[pSS] reported in the literature, PEDOT[polyABTS] exhibits the same color and level of electrochromic performance when a cathodic potential is applied. The doping of PEDOT with polyABTS instead of pSS, however, contributes an additional electrochromic state without a loss in electrochromic performance. This work demonstrates a general approach to achieving multielectrochromic materials by codeposition of a conductive polymer with a redox-active polymer.

Experimental Procedures

Chemicals and Electrodes. Chemicals used to prepare the electrolyte, 3,4-ethylenedioxythiophene (EDOT), and pyrrole were purchased from Aldrich and used without further purification. Synthesis of polyABTS followed a literature procedure.⁴⁰ Working electrodes (50 mm \times 10 mm \times 1.5 mm) were fabricated from glass slides (150 mm \times 150 mm \times 1.5 mm) coated with ITO (Delta Technology, Ltd.). An Ag/AgCl reference electrode was used, and potentials are reported accordingly.

Electrosynthesis of Polymer Films. Films of PEDOT[polyABTS] for electrochromic measurements were electrosynthesized from aqueous solutions containing 15 mM EDOT and 2 mg/mL polyABTS. Electrodeposited films covered an area of 35 mm \times 10 mm on ITO slides that were 50 mm \times 10 mm \times 1.5 mm. Thin films were electrosynthesized by sweeping the potential from 0 to 1 V for 50 cycles, and thick films were electrosynthesized by sweeping the potential from 0.4 to 1 V for 50 cycles.

Equipment and Measurements. An EG&G Potentiostat/Galvanostat, model 263A, was used to electrodeposit films of PEDOT[polyABTS] and PEDOT[pSS] onto the working electrode and to measure the electrochemical properties of deposited films. The counter electrode was platinum mesh, and the reference electrode was Ag/AgCl. UV-vis spectra of films of PEDOT[polyABTS] on ITO were measured using a dual beam Cary-500 scanning spectrophotometer with matched quartz cuvettes (3 mL capacity, 1 cm pathway length) filled with 0.2 M KCl. The thickness of films of polyABTS, PEDOT[polyABTS], and PEDOT[pSS] was measured using white-light interferometry (ZYGO Nearview 5000 3-D).

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