Dual-Polymer Electrochromic Film Characterization Using Bipotentiostatic Control

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We report an analytical method which allows the systematic variation of color states of pairs of electrochromic conjugated conducting polymers with simultaneous spectroelectrochemical and colorimetric characterization of the resulting color summation. This method measures colors by transmitting light through two polymer films stacked together in electrolyte and under separate potentiostatic control. The polymers that were used in this work are poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-propylenedioxypyrrole) (PProDOP), and dihexyl-substituted poly(3,4-propylenedioxythiophene) (PProDOT-Hx_2). These are all cathodically coloring polymers, PEDOT switching from a transmissive sky blue to a deep blue, PProDOP switching from a highly transmissive gray/blue to a brown and then to an orange, and PProDOT-Hx_2 switching from a transmissive sky blue to a purple/magenta color upon reduction. Coupling these polymers logically by the dual-polymer electrochromic film characterization technique led us to obtain new colors which were not observed when these polymers were studied separately. For example, coupling PEDOT and PProDOP films in their neutral state resulted in a new red/brown color ($L^* = 59$, $a^* = 25$, and $b^* = 50$), which is different from the original colors these polymers show in their neutral states, deep blue ($L^* = 64$, $a^* = -5$, and $b^* = -37$) and orange ($L^* = 76$, $a^* = 31$, and $b^* = 75$), respectively. A full palette of colors is accessible by coupling existing electrochromic polymers by this new bipotentiostatic technique.

Introduction

Electrochromism is a change, evocation, or bleaching of color as effected either by an electron-transfer (redox) process or by a sufficient electric potential.[1] In many applications it is required to be reversible. Visible electrochromism is, of course, only useful for display purposes if one of the colors is markedly different from the other, as for example when the absorption band of one redox state is in the visible region of the electromagnetic spectrum while the other is in the UV. If the colors are sufficiently intense and different, then the material is said to be electrochromic, and the species undergoing change is usefully termed an "electrochrome".[1] Many chemical species show electrochromic properties,[1–8] including metal coordination complexes (both in solution and as polymer films), inorganic charge-transfer complexes, metal oxides (especially tungsten trioxide, WO_3), viologens (4,4′-bipyridylium salts), and conjugated conducting polymers such as polypyrroles and polythiophenes.

Conjugated conducting polymers receive particular attention for their potential use in controllable light-reflective or light-transmissive electrochromic displays for optical information and storage.[8] They have fast switching speeds, high contrast ratios, and high coloration efficiencies. Several are available as solution-processable materials, and their electrochromic properties and color states can be synthetically tuned.[9] In the oxidized state, conjugated conducting polymers are charge-balanced, "doped", with counteranions ("p-doping") and have a delocalized π-electron band structure.[10] Reduction of "p-doped" conjugated conducting polymers, with concurrent counteranion exit (or electrolyte cation incorporation) yields the '"undoped" (neutral) electrically insulating form. The electronic bandgap (E_g), defined as the energy difference between the highest occupied π-electron band (valence band) and the lowest unoccupied band (the conduction band), determines the intrinsic optical properties. The color change or contrast between doped and undoped forms of the polymer depends on the magnitude of the

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bandgap of the undoped polymer. Thin films of conjugated conducting polymers with E_g greater than 3 eV (~400 nm) are colorless and transparent in the undoped form, while in the doped form they generally absorb visible radiation. Those with $E_g \leq$ 1.8–1.9 eV (~650–700 nm) tend to be highly absorbing in the undoped form, but after doping, the free carrier absorption is relatively weak in the visible region as it is transferred to the near-infrared (NIR). Polymers with intermediate gaps have distinct optical changes throughout the visible region and can exhibit several colors. Through bandgap control, achieved primarily through main-chain and pendant group structural modification, the accessible color states in both the doped (conductive) and neutral (insulating) forms of a conjugated conducting polymer can be varied,[9] with both cathodically coloring and anodically coloring electrochromes being available.

Examples of cathodically coloring conjugated conducting polymers are those based on poly(3,4-ethylenedioxythiophene) (PEDOT), which has a low bandgap of 1.6–1.7 eV. Neutral PEDOT appears deep blue and switches to a transmissive blue state. As PEDOT and its alkyl derivatives are cathodically coloring, these electrochromes are suitable for use with anodically coloring conjugated conducting polymers in the construction of dual polymer electrochromic devices (ECDs).[11] With a blue-shifted absorption, poly(3,4-ethylenedioxypyrrole) (PEDOP) exhibits a bright red color in its neutral state (bandgap 2.05 eV) and a light blue transmissive state upon oxidation, retaining a cathodically coloring capability. Upon increasing the ring size of the alkylene bridge, the neutral form of poly(3,4-propylenedioxypyrrole) (PProDOP)[12] is an orange color, passes through a brown color upon intermediate doping, and finally to a light gray/blue color upon full oxidation.

The ability to perform substitution at the nitrogen in the PXDOP family has allowed the creation of higher bandgap polymers while maintaining their low oxidation potentials.[13] This substitution induces a twist in the polymer backbone, which results in a decrease of the effective π-conjugation, and an increase in the bandgap, resulting in a blue shift of the $\pi-\pi^*$ transition, with the intragap polaron and bipolaron transitions occurring in the visible region. As such, these materials are anodically coloring. The nature of the substituent has an effect on the extent to which the $\pi-\pi^*$ transition is shifted. For *N*-methyl PProDOP the bandgap occurs at 3.0 eV, compared to 2.2 eV for PProDOP.[13] Both *N*-[2-(2-ethoxyethoxy)ethyl] PProDOP (*N*-Gly PProDOP) and *N*-propanesulfonate PProDOP (*N*-PrS PProDOP) are colorless when fully reduced and colored upon full oxidation.[13]

ECDs are designed to modulate absorbed, transmitted, or reflected incident electromagnetic radiation through the application of an electric field across the electrochromic materials within the device.[8] Often, an ECD includes two electrochromic materials that have complementary optical (cathodic and anodic coloring) properties allowing both electrochromes to contribute to the optical response of the device. The absorptive/transmissive-type ECD operates with a reversible switching of the electrochrome between a colored state and a bleached state. Both working and counter electrode are transparent so that light can pass through the device. Reflective ECDs have also been developed where the active electrochromic polymer is deposited onto an outward-facing reflective electrode, such as gold deposited onto a flexible, ion permeable substrate.[14]

Although choice of electrochromic conjugated conducting polymers can provide colors across the entire range of the visible spectrum, the evocation of colors through color addition, especially in intermediate oxidation states, is not always obvious in dual polymer additive devices. Here, we introduce a novel analytical method, which allows the systematic variation of color states of pairs of electrochromic conjugated conducting polymers with simultaneous spectroelectrochemical and colorimetric characterization of the resulting color summation. In this method, the polymers are prepared as films on ITO/glass substrates and mounted back-to-back in transmission mode in a spectroelectrochemical cell. A bipotentiostat provides separate electrochemical control of individual polymer color states. By the dual-polymer electrochromic technique through bipotentiostatic control, we demonstrate the generation of new color states by coupling existing polymers. Our choices of polymers for study, with examples prepared by both monomer electropolymerization and the spray-coating of soluble polymers,[15] have been from the available poly(3,4-alkylenedioxythiophene) (PXDOT) and poly(3,4-alkylenedioxypyrrole) (PXDOP) families, although, in principle, this approach is applicable to numerous electrochromes.

Results and Discussion

In its simplest sense, color mixing allows the matching of complex colors through the combination or formulation of color components.[16,17] In the dual-polymer electrochromic film characterization technique reported here, the results can be used to design dual polymer ECDs where the color summation of the films in any of their color states can be accessed as the films oxidation states are controlled independently. The key to this is understanding the coloration process during the doping/dedoping of the polymer films. These "primary" colors can be summed to more complex colors by passing white light simultaneously through two films and observing the transmitted light. Color engineering for ECDs will let us foresee colors that are accessible after the primary components are matched logically. Each dual system will have a palette of colors available made possible by independently varying the oxidation state of the two films.

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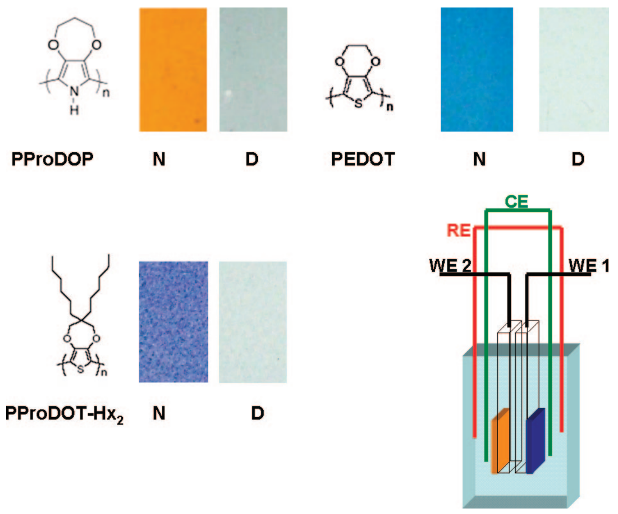

Figure 1. Chemical structures of the polymers that are used in dual-polymer electrochromic method and the photographs of their neutral (N) and doped (D) states with the schematic of the dual-polymer electrochromic characterization cell.

In this work we have used PEDOT, PProDOP, and dihexyl-substituted poly(3,4-propylenedioxythiophene) (PProDOT-Hx$_2$) as exemplary EC polymers whose colors can be summed to provide new colors not possible with the single films alone.[15,18] The repeat unit structures of the polymers, along with photographs of the polymer films in their oxidized and reduced states, are shown in Figure 1. Each of these polymers is cathodically coloring with blue, orange, and purple/magenta colors in their fully neutral states.

Also shown in Figure 1 is a schematic of the cell used for the dual-polymer EC characterization method. In this construction, EC polymer films are deposited onto separate ITO/glass slides and placed back-to-back in a cuvette in order to mimic the combined light absorption properties of a dual polymer ECD. The redox state of each film (WE 1 and WE 2) is then controlled independently with a bipotentiostat relative to a reference, allowing the full range of accessible optical states of each polymer to be set. Spectroscopic and colorimetric characterization of the dual film system thus allows a palette of colors to be obtained where the sum of the two films optical can be monitored.

Understanding the coloration process during the oxidation and charge neutralization of the polymer films is of paramount importance in establishing the new color palettes. To understand this fully, it is necessary to obtain the electrochemical and optical properties of the separate polymer films. Electrochemical characterizations on Pt-button electrodes and spectroelectrochemical experiments on ITO-coated glass electrodes were used to establish baseline properties.

In order to obtain thin films of the EC polymers, both EDOT and ProDOP were electrochemically polymerized onto Pt-button electrodes from a 0.1 M lithium perchlorate ($LiClO_4$)/propylene carbonate (PC) solution containing 10 mM monomer by repeated scanning, as shown in the insets of Figures 2 and 3, respectively. During the first anodic scans, a single peak was observed corresponding to irreversible oxidation of the monomers, indicating formation of radical cations. The peaks of monomer oxidation are observed at +1.02 V for EDOT and +0.56 for ProDOP vs Fc/Fc$^+$. (All further potentials will be reported versus this reference electrode.) Subsequent scanning shows evolution of a redox response at lower potentials attributed to the polymer oxidation and charge neutralization. PProDOT-Hx$_2$ was drop-

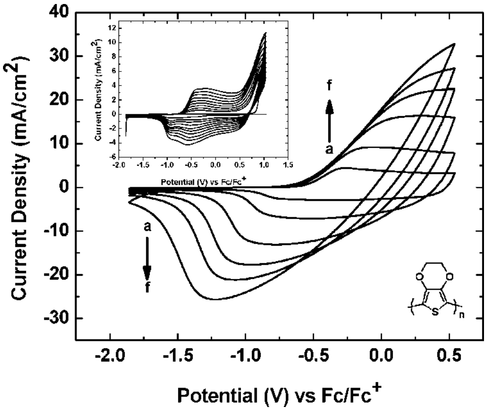

Figure 2. Cyclic voltammograms of PEDOT in 0.1 M $LiClO_4$/PC at scan rates of (a) 20, (b) 50, (c) 100, (d) 150, (e) 200, and (f) 300 mV/s. The left top inset shows the repeated potential scanning electropolymerization of EDOT from 0.01 M monomer in 0.1 M $LiClO_4$/PC solution on a Pt-button electrode at a scan rate of 20 mV/s.

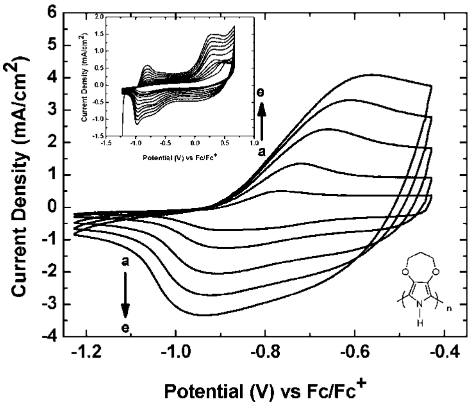

Figure 3. Cyclic voltammograms of PProDOP in 0.1 M $LiClO_4$/PC at scan rates of (a) 20, (b) 50, (c) 100, (d) 150, and (e) 200 mV/s. The left top inset shows the repeated potential scanning electropolymerization of ProDOP from 0.01 M monomer in 0.1 M $LiClO_4$/PC solution on a Pt-button electrode at a scan rate of 20 mV/s.

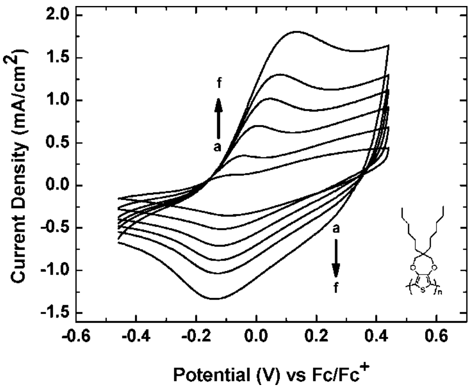

Figure 4. Cyclic voltammograms of PProDOT-Hx$_2$ in 0.1 M $LiClO_4$/PC at scan rates of (a) 20, (b) 50, (c) 100, (d) 150, (e) 200, and (f) 300 mV/s. Film prepared by drop-casting onto a Pt-button electrode from 5 mg/mL polymer/toluene solution.

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cast from a 5 mg/mL polymer/toluene solution onto a Pt-button electrode after being filtered through 0.20 μm PTFE filter.

After deposition, all films were rinsed with monomer-free electrolyte solutions, and cyclic voltammograms (CV's) were recorded at scan rates ranging from 20 to 300 mV/s, as shown in Figures 2–4. A linear increase of the current with scan rate is observed for each film, indicative of a surface-adhered electroactive polymer film. An important aspect observed in these experiments is that the current passing through the PEDOT film is an order of magnitude greater than the current passing through the PProDOP (prepared with the same number of deposition scans) and PProDOT-Hx$_2$ films. This demonstrates the highly effective electropolymerization and switching characteristics of PEDOT. This shows that during the preparation of dual film devices it is important to balance the overall amount of electroactive polymer on each electrode, usually using film thickness as the operational parameter, in order to obtain a balanced optical response.

Using the above CV experiments as a means of determining the correct potential ranges for switching and evaluating the stability of the electroactivity of the polymer films, spectroelectrochemical and colorimetric experiments were conducted to elucidate the separate optical characteristics of the polymer films alone. Films were deposited on ITO coated glass slides potentiostatically for PEDOT (1.6 V for 20 s), galvanostatically for PProDOP (0.11 mA for 1000 s), and by spray-casting (5 mg/mL from toluene) for PProDOT-Hx$_2$. The film thicknesses were adjusted to between 100 and 300 nm so that the absorbances of the polymer films at $\lambda_{\max}$ in their neutral states were equal. The spectroelectrochemical series for each of the polymer films are shown in Figure 5. In their neutral states, PEDOT appears deep blue (absorbing between 1.6 and 2.8 eV), PProDOP appears orange (absorbing between 2.2 and 3.0 eV), and PProDOT-Hx$_2$ appears purple (absorbing between 1.8 and 3.0 eV). As these polymer films are doped, charge carrier states emerge with the majority of the light absorption for each polymer being in the near-infrared, which results in highly transmissive films. Note, in the spectroelectrochemical series for PProDOP, we step to +0.5 V, which is substantially higher than the potential window used in the CV. This higher applied potential allowed us to fully oxidize the film and attain the most transmissive form. This ability to form a transmissive state for each of these cathodically coloring polymers is important when considering them for use in EC displays and absorption/transmission windows. Converting to transmittance, we note that $\Delta\%T$ values at $\lambda_{\max}$ (632, 522, and 571 nm) are 55%, 73%, and 65% for PEDOT, PProDOP, and PProDOT-Hx$_2$, respectively.

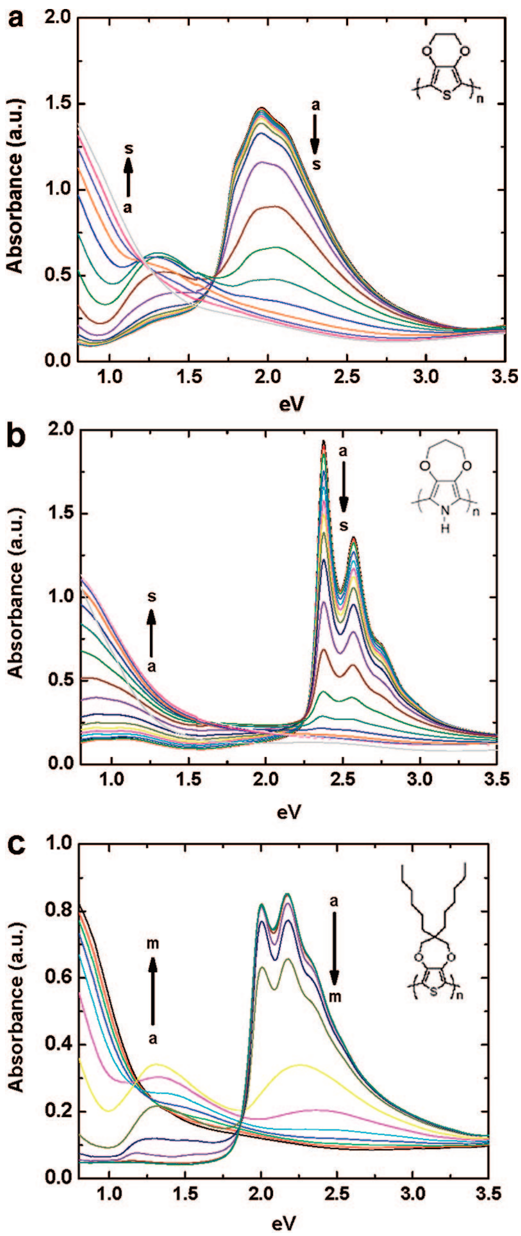

Figure 5. Spectroelectrochemistry of (a) potentiostatically deposited, redox-switched, PEDOT film at applied potentials of (a) −1.45 to (s) +0.35 V vs Fc/Fc$^+$ in increments of 0.1 V, (b) galvanostatically deposited, redox-switched, PProDOP film at applied potentials of (a) −1.7 to (s) +0.1 V vs Fc/Fc$^+$ in increments of 0.1 V, and (c) spray-cast, redox-switched, PProDOT-Hx$_2$ film at applied potentials of (a) −0.67, (b) −0.57, (c) −0.47, (d) −0.37, (e) −0.27, (f) −0.17, (g) −0.07, (h) +0.03, (i) +0.13, (j) +0.23, (k) +0.33, (l) +0.43, and (m) +0.53 V vs Fc/Fc$^+$.

Since color is subject to the response, sensitivity, and perception of the human eye, elaboration on EC properties is best accomplished with an accurate quantitative measure of the color. *In situ* color coordinates (hue and saturation) and relative luminance (the amount of light transmitted through the polymer film) values were recorded for each polymer film separately (Figure 6). Considering the three polymer films in their fully reduced forms, PEDOT has a^* and b^* values of –5 and –37, respectively, giving it a dark blue color with a relative luminance of 32%, PProDOP has a^* and b^* values of 31 and 75, giving it an orange color with a relative luminance of 50%, and PProDOT-Hx$_2$ has a^* and b^* values of 14 and −45, giving it a purple color with a relative luminance of 24%. Note there is variability in the measured L^*, a^*, and b^* values measured as a function of subtle changes in film thickness and applied potential. For example, in earlier work we measured neutral PEDOT as $L^* = 20$, $a^* = 15$, and $b^* = -43$.[19] While in both instances the PEDOT films are obviously a deep blue, this points out the sensitivity of the method.

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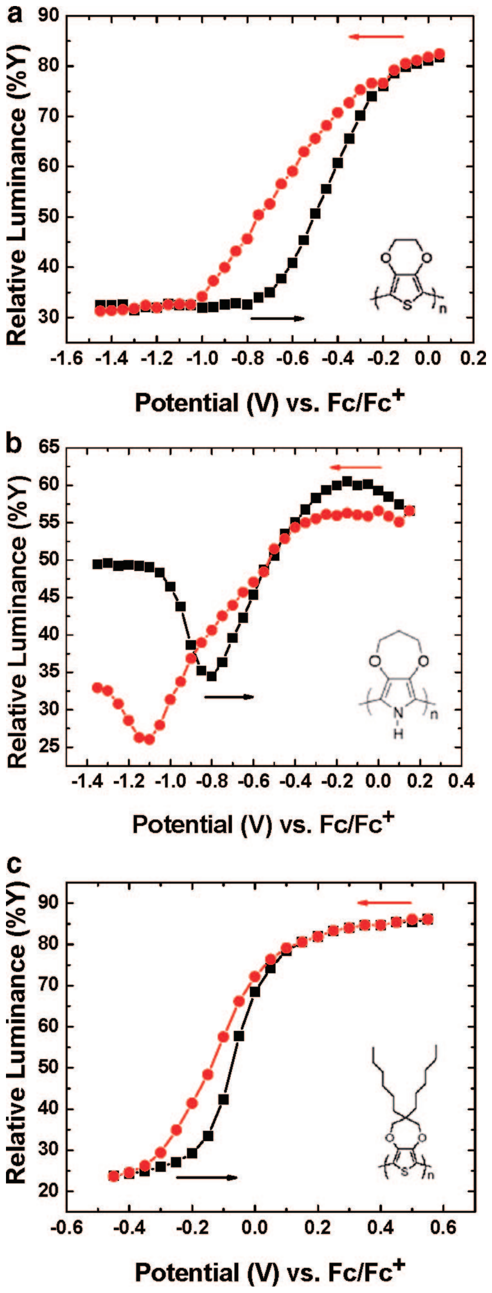

Figure 6. Relative luminance as a function of applied potential of (a) PEDOT, (b) PProDOP, and (c) PProDOT-Hx$_2$.

When the films are completely oxidized, they all are converted into highly transmissive and sky-blue films. Now, PEDOT exhibits *a** and *b** values of –2 and –4, respectively, with a relative luminance of 82%, PProDOP exhibits *a** and *b** values of –3 and –6 with a relative luminance of 57%, and PProDOT-Hx$_2$ exhibits *a** and *b** values of –2 and –4 with a relative luminance of 86%, demonstrating the cathodic coloration properties of each of these polymers.

As shown by the luminance change in Figure 6c, PProDOT-Hx$_2$ possesses the highest contrast ratio in the visible region of the three polymers studied, having $\Delta\%Y$ of 62% while PEDOT and PProDOP have 50% and 10–20% (from fully neutral to the oxidized form), respectively. The reduced contrast of PEDOT relative to PProDOT-Hx$_2$ is due to the strong NIR absorption that is found in the oxidized form of PEDOT, providing a visible light absorption tail in the red region of the spectrum which is lower in intensity for the substituted PProDOTs.[15] The simple loss of absorption in the visible for the thiophene derivatives upon oxidation is seen to be more complicated in PProDOP. As the polymer has a higher band gap, the neutral form is more transmissive to visible light than either of the thiophene derivatives. The initial formation of a polaron during oxidation gives an absorption in the visible region which results in an initial loss of luminance (Figure 6b). This polaron absorption is subsequently bleached upon full oxidation, and a highly transmissive ($\%Y \sim 60\%$), light gray state is ultimately reached. These luminance changes with applied potential will play a strong role in the EC response of the dual film systems to be described below.

Tandem chronoabsorptometry and chronocoulometry experiments allow calculation of composite coloration efficiency (CE, the change in optical density as a function of charge passed) values as a practical method of CE determination. By choosing 95% of the optical density change, the transmittance of the reduced films is compared to that of the oxidized films. The amount of time to reach 95% of the full optical density is chosen as nearly all of the optical change has occurred, and a direct comparison of polymers that switch at different rates can be made.[20] Polymer films with similar switching times and contrast ratios were chosen for application to the dual-film technique. The coloration efficiency for PEDOT is 280 cm^2/C and the 95% switch time is 1.7 s with a charge density of 3.4 mC/cm^2, while for PProDOP the coloration efficiency is 224 cm^2/C and the 95% switch time is 0.9 s with a charge density of 1.6 mC/cm^2, and for PProDOT-Hx$_2$ the coloration efficiency is 519 cm^2/C and the 95% switch time is 0.6 s with a charge density of 1.4 mC/cm^2 (Figure 7). All three polymer films have substantial EC switching occurring in the subsecond time frame and are fully switched within 2 s at most.

Dual-Film Electrochromic Method. Absorbance spectra of PEDOT and PProDOP films were taken separately at reduced (both at −1.35 V vs Fc/Fc$^+$) and oxidized (PEDOT at +0.45 V and PProDOP at −0.05 V vs Fc/Fc$^+$) states, and these spectra were summed theoretically in order to attain a perspective of the combination of the optical response expected from the dual-film EC method. This is demonstrated by the single film red and black curves in Figure 8, along with the summation represented by the green curve (note the green curve in Figure 8a is difficult to see behind the blue curve).

Two ITO working electrodes with different EC polymer films on them were placed back-to-back in a 1 cm quartz cell, with a Ag wire reference electrode and Pt wire counter electrode, and placed under separate potentiostatic control (Figure 1). *In situ* color coordinates, relative luminance values, and spectra in the visible region were recorded from the dual-polymer devices upon application of varied potentials to the separate working electrodes in a 0.1 M lithium perchlorate/propylene carbonate solution. The blue curves in Figure 8 show the direct spectral response from the combined films. The theoretical and experimental spectra are

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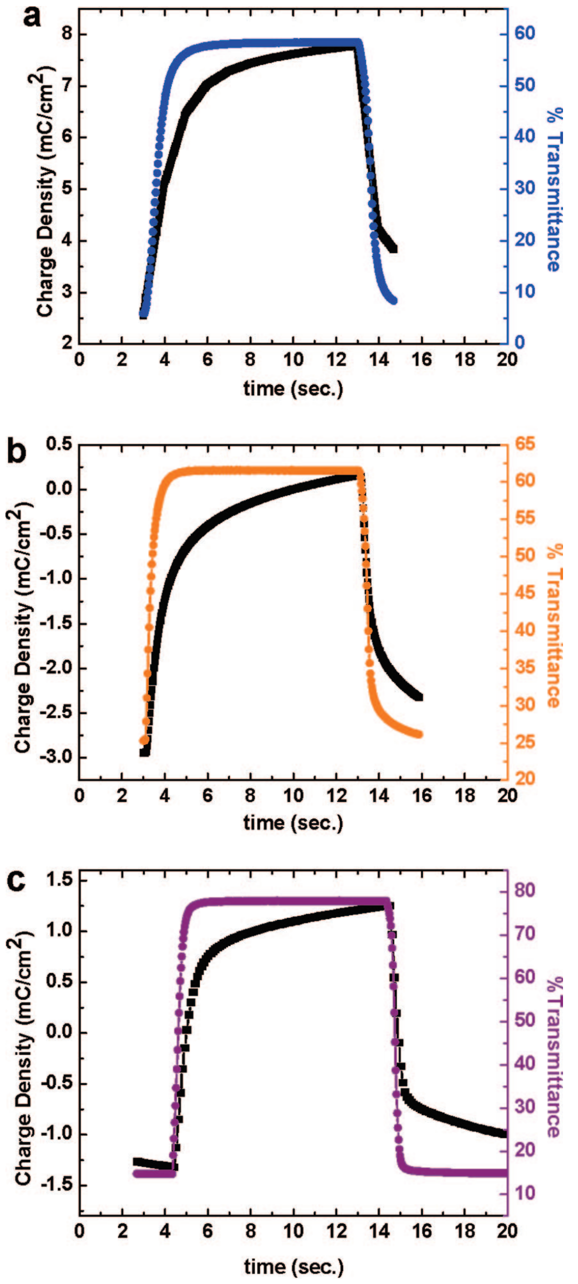


Figure 7. Tandem chronoabsorptometry and chronocoulometry experiments for (a) PEDOT (−1.45 to 0.55 V vs Fc/Fc$^+$, held for 10 s at each potential at 632 nm), (b) PProDOP (−1.7 to 0.1 V vs Fc/Fc$^+$, held for 10 s at each potential at 522 nm), and (c) PProDOT-Hx$_2$ (−0.67 to 0.53 V vs Fc/Fc$^+$, held for 10 s at each potential at 571 nm) in 0.1 M LiClO$_4$/PC solution.

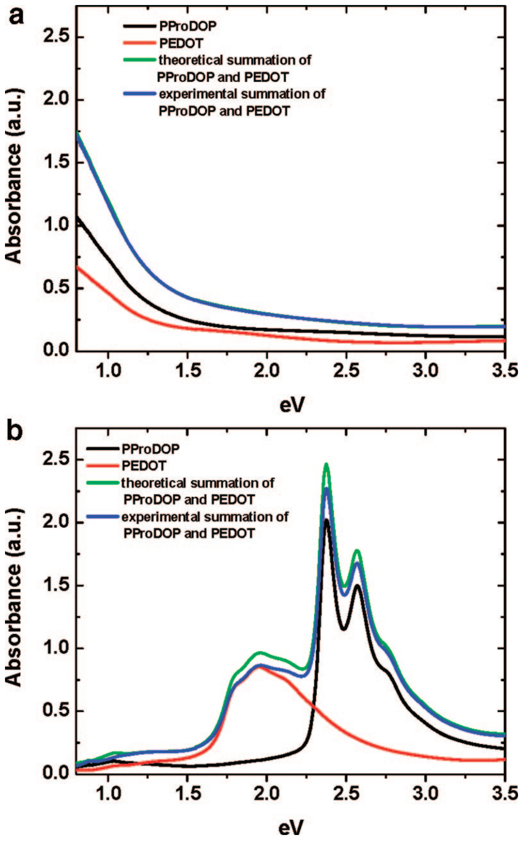
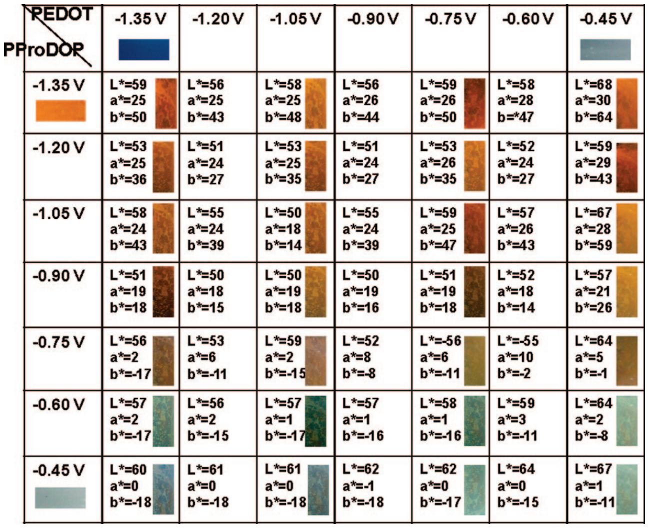


Figure 8. UV–vis−NIR spectra of the individual PProDOP and PEDOT films and the spectra of PProDOP/PEDOT from dual-polymer electrochromic setup at (a) oxidized and (b) reduced states in 0.1 M LiClO$_4$/PC solution.

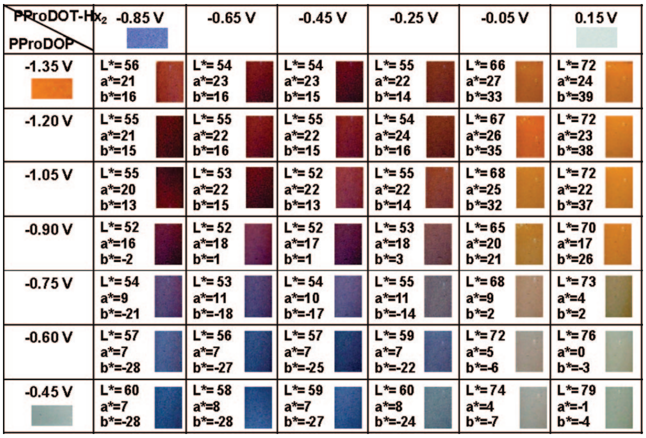


PEDOT / PProDOP	-1.35 V	-1.20 V	-1.05 V	-0.90 V	-0.75 V	-0.60 V	-0.45 V
-1.35 V	L*=59 a*=25 b*=50	L*=56 a*=25 b*=43	L*=58 a*=25 b*=48	L*=56 a*=26 b*=44	L*=59 a*=26 b*=50	L*=58 a*=28 b=*47	L*=68 a*=30 b*=64
-1.20 V	L*=53 a*=25 b*=36	L*=51 a*=24 b*=27	L*=53 a*=25 b*=35	L*=51 a*=24 b*=27	L*=53 a*=26 b*=35	L*=52 a*=24 b*=27	L*=59 a*=29 b*=43
-1.05 V	L*=58 a*=24 b*=43	L*=55 a*=24 b*=39	L*=50 a*=18 b*=14	L*=55 a*=24 b*=39	L*=59 a*=25 b*=47	L*=57 a*=26 b*=43	L*=67 a*=28 b*=59
-0.90 V	L*=51 a*=19 b*=18	L*=50 a*=18 b*=15	L*=50 a*=19 b*=18	L*=50 a*=19 b*=16	L*=51 a*=19 b*=18	L*=52 a*=18 b*=14	L*=57 a*=21 b*=26
-0.75 V	L*=56 a*=2 b*=-17	L*=53 a*=6 b*=-11	L*=59 a*=2 b*=-15	L*=52 a*=8 b*=-8	L*=-56 a*=6 b*=-11	L*=-55 a*=10 b*=-2	L*=64 a*=5 b*=-1
-0.60 V	L*=57 a*=2 b*=-17	L*=56 a*=2 b*=-15	L*=57 a*=1 b*=-17	L*=57 a*=1 b*=-16	L*=58 a*=1 b*=-16	L*=59 a*=3 b*=-11	L*=64 a*=2 b*=-8
-0.45 V	L*=60 a*=0 b*=-18	L*=61 a*=0 b*=-18	L*=61 a*=0 b*=-18	L*=62 a*=-1 b*=-18	L*=62 a*=0 b*=-17	L*=64 a*=0 b*=-15	L*=67 a*=1 b*=-11

Figure 9. *L*a*b* color coordinates and photography for PProDOP/PEDOT in 0.1 M LiClO$_4$/PC (all potentials are reported vs Fc/Fc$^+$).

shown to overlay one another completely for the oxidized films and are also quite similar for the reduced films. The color transmitted through the stacked films thus appears completely different from the component films and is difficult to foresee. The experimental summation spectrum proves that the dual system enables the physical addition of the optical properties of two different polymer systems thus motivating the perception of new colors which are the mixtures of each polymer.

Two dual-film systems were studied colorimetrically from the three polymer films employed. The color palettes in Figures 9 and 10 show the photographs and the *L*a*b* color coordinates as a function of the separate potential applied to each film. These color palettes can be used to tune in the accessible colors from a dual-film EC device. For example, as shown in Figure 9, as PProDOP is reduced and held in its orange state while sequentially oxidizing PEDOT, the luminance of the dual-film system increases from 59 to 68 as PEDOT is converted from a dark blue to a transmissive film. Along this track, the orange color dominates as the film retains an orange/brown hue. Holding PEDOT in the deep blue neutral state while sequentially oxidizing the PProDOP



PProDOT-Hx_2 / PProDOP	-0.85 V	-0.65 V	-0.45 V	-0.25 V	-0.05 V	0.15 V
-1.35 V	L*= 56 a*=21 b*=16	L*= 54 a*=23 b*=16	L*= 54 a*=23 b*=15	L*= 55 a*=22 b*=14	L*=66 a*=27 b*=33	L*=72 a*=24 b*=39
-1.20 V	L*= 55 a*=21 b*=15	L*= 55 a*=22 b*=16	L*= 55 a*=22 b*=15	L*= 54 a*=24 b*=16	L*=67 a*=26 b*=35	L*=72 a*=23 b*=38
-1.05 V	L*= 55 a*=20 b*=13	L*= 53 a*=22 b*=15	L*= 52 a*=22 b*=13	L*= 55 a*=22 b*=14	L*=68 a*=25 b*=32	L*=72 a*=22 b*=37
-0.90 V	L*= 52 a*=16 b*=-2	L*= 52 a*=18 b*=1	L*= 52 a*=17 b*=1	L*= 53 a*=18 b*=3	L*=65 a*=20 b*=21	L*=70 a*=17 b*=26
-0.75 V	L*= 54 a*=9 b*=-21	L*= 53 a*=11 b*=-18	L*= 54 a*=10 b*=-17	L*= 55 a*=11 b*=-14	L*=68 a*=9 b*=2	L*=73 a*=4 b*=2
-0.60 V	L*= 57 a*=7 b*=-28	L*= 56 a*=7 b*=-27	L*= 57 a*=7 b*=-25	L*= 59 a*=7 b*=-22	L*=72 a*=5 b*=-6	L*=76 a*=0 b*=-3
-0.45 V	L*= 60 a*=7 b*=-28	L*= 58 a*=8 b*=-28	L*= 59 a*=7 b*=-27	L*= 60 a*=8 b*=-24	L*=74 a*=4 b*=-7	L*=79 a*=-1 b*=-4

Figure 10. *L*a*b* color coordinates and photography for PProDOP/PProDOT-Hx_2 in 0.1 M $LiClO_4$/PC (all potentials are reported vs Fc/Fc^+).

yields a more distinct visual response with the brown/orange film changing to a green-tinted gray. Full oxidation of both films gives the lightest gray state.

The color changes are even more distinct in the PProDOP/PProDOT-Hx_2 couple seen in Figure 10. When the PProDOP film is held reduced while oxidizing the PProDOT-Hx_2 film, the luminance value increases from 56 to 72 due to the PProDOT-Hx_2 converting from dark purple to transmissive blue and resulting in a distinct reddish/purple to orange color change in the dual-film system. As the PProDOP is oxidized and the PProDOT-Hx_2 held reduced, the conversion to the blue state is observed as the PProDOP becomes highly transmissive. Finally, the highest luminance is observed as both films are oxidized and most transmissive.

Conclusion

This work demonstrates a new dual-polymer electrochromic film characterization technique allowing electrochromic polymer film couples to be studied and new colors generated. The color observed and thus the color coordinates read from the dual-polymer setup for the coupled polymer films were different than the data collected from these polymers when they were studied separately. For example, coupling PEDOT and PProDOP films in their neutral state resulted in a new color red/brown ($L^* = 59$, $a^* = 25$, and $b^* = 50$) which is totally different than the original colors these polymers show at their neutral states, dark blue ($L^* = 64$, $a^* = -5$, and $b^* = -37$) and orange ($L^* = 76$, $a^* = 31$, and $b^* = 75$), respectively. A full palette of colors is accessible by the logical coupling of electrochromic polymers in the dual-polymer electrochromic setup, and this method eliminates the need to synthesize new families of polymers to generate different colors. With the correct choice of materials, the dual system promises many intermediate colors which will enable the formation of a wide color scale for ECDs.

Experimental Section

Propylene carbonate was obtained from Acros Organics and lithium perchlorate was obtained from Aldrich, and they were used without further purification. EDOT was provided by H.C. Starck and distilled under vacuum from CaH_2. ProDOP was provided by CIBA Specialty Chemicals. PProDOT-Hx_2 was synthesized as previously described. [15] ITO-coated glass slides (7 × 50 × 0.7 mm, $R_s = 15\ \Omega/\square$) were obtained from Delta Technologies. Contact to the ITO slides was made using conductive Cu tape (1131) purchased from 3M.

The potentials for fundamental electrochemical studies, spectroelectrochemistry, and chronoabsorptometry were controlled by EG&G PAR model 273A potentiostat/galvanostat in a three-electrode cell configuration consisting of Ag wire pseudo-reference electrode, which was calibrated to the ferrocene/ferrocinium (Fc/Fc^+) redox couple, platinum button (0.02 cm^2), or ITO-coated glass slide as the working electrode and platinum wire as the counter electrode in a 0.1 M lithium perchlorate/propylene carbonate solution purged by argon. All absorption/transmission, spectroelectrochemistry, and chronoabsorptometry experiments were carried out on a Varian Cary 500 Scan UV–vis−NIR spectrophotometer.

Colorimetry was carried out using a Minolta CS-100 Chroma Meter, and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements. The sample was illuminated from behind by a D50 (5000 K) light source in a light booth designed to eliminate external light. The experimental setup used for colorimetric analysis of single polymer films is similar to the one used for spectroelectrochemistry. The applied potential is controlled either by an EG&G 273 potentiostat (for single films) or a Pine Bipotentiostat model AFCBP1 (for dual technique).

Dual Method. Both PProDOP and PEDOT were electropolymerized onto ITO-coated glass slides from a 0.1 M lithium perchlorate ($LiClO_4$)/propylene carbonate (PC) solution containing 10 mM monomer, galvanostatically and potentiostatically, respectively. PProDOT-Hx_2 was spray-coated from a 5 mg/mL polymer/toluene solution onto ITO-coated glass slide. The thicknesses of the films vary from 100 to 300 nm and measured by a Dektak 3030 surface profile measuring system purchased from Vecco Instruments, Inc. Both ITO electrodes with polymer films on them and under separate potentiostatic control were placed back-to-back in a 1 cm quartz cell, with a Ag wire as a reference electrode and a Pt wire as a counter electrode. ITO-coated glass slides were used as the working electrodes. *In situ* color coordinates, relative luminance values, and electromagnetic spectra in the visible region were recorded from the dual-polymer devices upon application of different potentials to different working electrodes in a 0.1 M lithium perchlorate/propylene carbonate solution.

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