In Situ Colorimetric Analysis of Electrochromic Polymers and Devices

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We report a colorimetric method for the in situ study of electrochromic polymers based on the CIE system of colorimetry. This method is useful for the comparison of the electrochemical and optical properties of conjugated polymers, and for gaining control of the color of dual polymer electrochromic devices. Twelve electrochromic polymers were investigated using in situ colorimetric analysis in order to define their CIE coordinates and electrochemical potential windows. By controlling the electron density and steric interactions along conjugated polymer backbones, we have developed a set of electrochromic polymers that provides colors throughout the full range of color space. The applicability of the method is illustrated with a model dual polymer device based on poly(2-(3,4-ethylenedioxy)thienyl-(biphenyl)) (PBEDOT-BP) and poly(3,6-bis(3,4-ethylenedioxy)thienyl)-*N*-methylcarbazole) (PBEDOT-NMeCz). This device yields green/brown colors ($L^* = 48$, $a^* = 0$, $b^* = 20$ and $L^* = 44$, $a^* = 6$, $b^* = 26$) interesting for earthtone and natural vegetation chameleon materials when the charge states of the two polymers are reversed. This technique is a convenient method for reproducibly fine-tuning the color of electrochromic materials, while reducing trial and error in the process of electrochromic device development.

Introduction

In the years that have followed the initial discovery of the high conductivity of poly(acetylene), the study of conducting and electroactive polymers has become a major field of research leading to a number of classes of polymers.[1] This is driven by the possibility that these materials will be used in the development and improvement of various technological applications among which are the following: batteries, sensors, corrosion protection, transparent conductors, light-emitting diodes, mechanical actuators, artificial muscles, and electrochromic devices.[2] For such applications as switchable windows and mirrors, active advertising displays, and dynamic camouflage, electrochromic devices based on conducting polymers have become a recent focus of research. This is due in part to the fact that all electroactive and conducting polymers are potentially electrochromic materials, are more processable than inorganic electrochromic materials, and offer the advantage of a high degree of color tailorability.[3] This tailorability has been achieved through the modification of various polymer systems via monomer functionalization and copolymerization, as well as with the use of blends, laminates, and composites.[1,4−8] Complex colors are achieved by mixing two existing colors in a dual polymer device.

For any colored material to be useful in a commercial product, specific colors are often required (color matching), which can be defined through colorimetry and expressed in various color spaces.[9] However, the determination of the resulting color in such devices is often the result of trial and error. Considerable effort in our group has been focused on building the "toolbox" for polymer electrochromic devices. Much of our work has been centered on the synthesis of numerous new conjugated polymer systems for electrochromic applications. In this paper, we report the development of a convenient method which allows the precise control of color in electrochromic devices using the many polymers available.

Electrochromism in Conducting Polymers. Electrochromism can be defined as a reversible and visible change in the transmittance and/or reflectance of a material as the result of electrochemical oxidation or reduction.[10] The property of electrochromism is not unique to conducting polymers but is found in a variety of materials; organic and inorganic alike.[11,12] In conju-

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gated electroactive polymers (commonly termed conducting polymers due to the fact that they can attain high conductivities in the doped state), electrochromic changes are induced by redox processes which are accompanied by ion insertion/expulsion and result in a modification of the polymer's electronic properties giving rise to changes in the color of the material. The color exhibited by the polymer is closely related to the band gap.[6] A major focus in the study of electrochromic polymeric materials has been that of controlling their colors by main-chain and pendant group structural modification. Polyheterocycles have proven to be of special interest for this due to their environmental stability under ambient and use conditions.[5]

Three major strategies of color control are used with electrochromic polymers. The polymer's band gap (defined as the onset of the π to π^* transition) is directly related to the relative energies of the HOMO and the LUMO. By judiciously substituting the polymer's repeat unit, the electrochromic properties can be controlled by the induced steric and electronic effects.[1,4,5,13−16] These substituents determine the effective conjugation length and electron density of the polymer backbone. Copolymers offer a second means of controlling the electrochromic properties of conducting polymers.[3,7,17−21] Copolymerization of distinct monomers, or homopolymerization of hybrid monomers containing several distinct units, can lead to an interesting combination of the properties observed in the corresponding homopolymers. Indeed, it has been observed that the color of copolymers based on carbazole, thiophene, and pyrrole derivatives can be controlled by altering the ratio of the respective monomers.[8] Blends, laminates and composites offer a third method, similar to copolymers, for combining the electrochromic properties of several systems. The use of two polymers covering different color regions is a simple way to achieve multi-color electrochromic devices.[3,8,21−26]

Colorimetric Analysis. There are three types of electrochromic devices (transmission/absorption, specular reflection/absorption, and diffuse scattering/absorption)[27] which either alter the color of the light that is transmitted or reflected by the device.[12] A number of research publications and reviews have been published concerning the construction of electrochromic devices.[25,28−37] To obtain controlled color states in these systems, the use of colorimetric analysis allows a "fine tuning" of the color. This is attained using available polymer systems, thus altering the electrochromic properties of the device without changing the molecular structure of the electrochromic polymer.

To a great extent, color is a subjective phenomenon causing the description of color, or the comparison of two colors, to be difficult. Much effort has been given to transforming the description of color from a subjective matter to an objective, quantitative nature, which is the focus of colorimetry.[38] Accordingly, there are three attributes that are used to describe color.[39] The first attribute identifies a color by its location in the spectral sequence: i.e., what wavelength of light is associated with this color. This is known as hue, dominant wavelength, or chromatic color. The second attribute is known as saturation, chroma, tone, intensity, or purity. This attribute deals with the level of white and/or black. The third attribute is the brightness of the color, and it is also referred to as value, lightness, or luminance.

To assign a quantitative scale to color measurement, these three basic attributes must be defined in a given color system. Many color systems exist,[40] but the most commonly used is the system established by The Commission Internationale de l'Eclairage (International Commission on Illumination) commonly known as the CIE system of colorimetry.[41] The CIE-defined color-matching functions are used to calculate the tristimulus values (X, Y, and Z), which are used to define all of the recommended color spaces.[40] These values take into account the manner in which the human eye perceives color. Color spaces can be defined as geometric constructs that contain all possible colors in a systematic manner according to the three attributes[38] and are the means by which the information on the tristimulus values is represented graphically either in two or three-dimensional space. The three most commonly used CIE color spaces are the 1931 Yxy, the 1976 $L^*u^*v^*$, and the 1976 $L^*a^*b^*$ systems.

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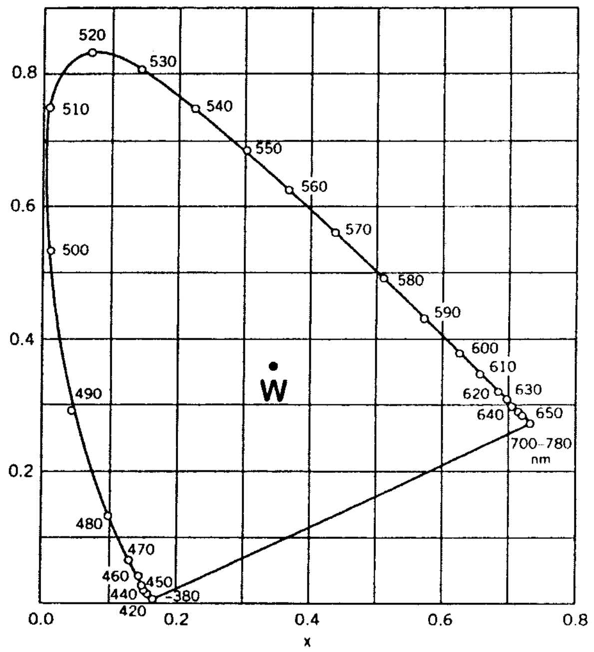

Figure 1. CIE 1931 *xy* chromaticity diagram with labeled white point.

In the CIE 1931 *Yxy* color space, the tristimulus value *Y* is defined as a measure of the brightness or luminance of the color. A two-dimensional *xy* representation is utilized, known as the chromaticity diagram in which *x* and *y* are calculated from the tristimulus values. When this relationship is examined in Figure 1, the line surrounding the horseshoe-shaped area is called the spectral locus, and on it are found the wavelengths of light in the visible region. The purple line connects the longest and shortest wavelengths across the base. Surrounded by the spectral locus and the purple line is the region known as the color locus, which contains every color. The point **W** within this locus is known as the white point, and its location is dependent on the light source used in either reflection or transmission experiments. The location of a point on the *xy* diagram gives the hue and saturation of the color. The hue is determined by drawing a straight line through the white point and the point of interest to the spectral locus thus obtaining the dominant wavelength of the color. For points lying along the purple line, a straight line containing the point, the white point, and the purple line is reflected back through the white point to the spectral locus, yielding the dominant wavelength of the complementary color.[9] The most saturated colors lie along the spectral locus and the purple line.[40] However, it is important to realize that the CIE 1931 color space does not associate any specific color with any point on the diagram.[39] This is due to the fact that the relative lightness or darkness of a color (its luminance) is important in how it is perceived.[38] The luminance (Y) is most often presented as a percentage relative to the background luminance (Y_0) [9] as found in eq 1. In 1976,

$$\% \; Y = \frac{Y}{Y_0} \times 100 \qquad (1)$$

the CIE introduced the $L^*a^*b^*$ and $L^*u^*v^*$ uniform color spaces.[40] However the 1931 *xy* chromaticity diagram is the most recognized method in which color is represented. The diagram conveys information in a straightforward manner, and hence it is very easy to use and understand. In addition, the CIE 1931 system is useful in that it can be used to analyze color in many different ways. Notably, the system can be used to predict the outcome of color mixtures.[38] The mixture of two colors is known to lie along the straight line connecting the points representing the colors on the *xy* chromaticity diagram. The position of the point depends on the ratio of the amounts of the two mixed colors. Considering all of the assets and drawbacks of these three different color spaces, the results to be reported in this paper will be expressed graphically in the CIE 1931 *Yxy* color space. Because of the common use of the $L^*a^*b^*$ color system in industry, these values are also reported.

Colorimetry of Electrochromic Materials. Colorimetry has been used to investigate the properties of electrochromic and light-emitting polymers, blends, and laminates.[3,8,22,25,42−45] Within copolymers, correlations can be found between the monomer ratio and $L^*a^*b^*$ color coordinates.[3] One study of the electrochemical processes in polyaniline, poly(*N*-methylpyrrole), and polythiophene using colorimetry involved in situ reflectance spectroelectrochemistry in conjunction with cyclic voltammetry.[42] It was found that, at various applied potentials, changes in the absorbance spectra corresponded to peaks in the cyclic voltammograms, as well as sharp turns in the CIE chromaticity diagram. Linear trajectories were concluded to represent single electrochemical processes. In this study, the colorimetric measurements appeared to be a reliable tool for representing changing electrochemical processes. Moreover, when compared to spectroelectrochemistry, such measurements were found to offer the distinct advantage of allowing one to plot spectral changes over the entire visible region with a single trace on a single graph.

For the study of the optical properties of electrochromic polymers, spectroelectrochemistry has been the preferred technique. This method, however, presents several practical problems including the facts that spectrophotometers are large and far from portable, and the sample cannot be visually monitored while the spectra are being recorded. A majority of the colorimetric studies of electrochromic materials published rely on the use of reflectance measurements made by a spectrophotometer, but such a method offers no real advantage over transmission spectroelectrochemistry for the study of optical properties.

Here we report a method for the study of the electrochromic properties of electroactive polymers. Our approach is different from those previously published[21,22] in that we have utilized colorimetric analysis for investigating the light transmission properties of electrochromic polymers in addition to studying their color. The inclusion of detailed luminance measurements sets our colorimetric study apart, makes our method directly applicable to transmittance-based electrochromic de-

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Table 1. Experimental Conditions Used for the Deposition of the Polymer Films

polymer	deposition method	Q_d (mC/cm^2)	electrolyte/solvent	ref
PEDOT (**1**)	galvanostatic, 3.0 mA/cm^2	50	0.1 M TBAP/ACN	*a*
PProDOT−(CH$_3$)$_2$ (**2**)	galvanostatic, 3.0 mA/cm^2	50	0.1 M TBAP/ACN	49, 50
P3MT (**3**) doped	galvanostatic, 7.5 mA/cm^2	100	0.1 M TBAP/ACN	*a*
PBTB−(OMe)$_2$ (**4**)	potentiostatic +1.18 V vs Ag/Ag$^+$	50	0.1 M TBAP/ACN	51
PEDOP (**5**)	galvanostatic, 0.05 mA/cm^2	50	0.1 M TBAP/ACN	47
PProDOP (**6**)	galvanostatic, 0.05 mA/cm^2	50	0.1 M LiClO$_4$/PC	47
PProDOP−CH$_3$ (**7**)	galvanostatic, 0.05 mA/cm^2	50	0.1 M LiClO$_4$/PC	47
PProDOP−(CH$_3$)$_2$ (**8**)	galvanostatic, 0.05 mA/cm^2	50	0.1 M LiClO$_4$/PC	47
PBuDOP (**9**)	galvanostatic, 0.05 mA/cm^2	50	0.1 M LiClO$_4$/PC	47
PBEDOT-NMeCz (**10**)	potentiostatic +0.73 V vs Ag/Ag$^+$	50	0.1 M LiClO$_4$/PC	46
PBEDOT-BP (**11**)	potentiostatic +0.83 V vs Ag/Ag$^+$	50	0.1 M TBAP/ACN	52
LPEB (**12**)	solution cast/ 2% in CHCl$_3$	N/A	0.1 M TBAP/ACN	53

[a] This work.

vices, and allows us to take full advantage of the predictive information that can be aquired from a chromaticity diagram. Like others,[21] our measurements are carried out using a small, portable device. However, unlike spectrophotometers, our use of a colorimeter allows us to select and vary the illuminating conditions and the simplified setup allows measurements to be made in almost any setting. These measurements offer additional information to that which can be obtained by spectroelectrochemistry. A colorimeter offers the asset of continuous visual sample monitoring and it allows one to test a material in an application specific manner by making either reflectance or transmittance measurements. In this study we considered the materials for their electrochromic applications such as smart windows. Therefore, a transmittance setup was preferred.

Results and Discussion

The chemical structures of the polymers studied using our new colorimetric method are presented in Figure 2 along with the various $L^*a^*b^*$ colors exhibited by the polymers. All of the polymers, with the exception of LPEB (**12**), which was cast from solution, were electrochemically deposited on ITO to nearly the same thickness (ca. 0.2 μm) to avoid ambiguities in the colorimetric measurements.[39] All of the polymers are listed in Table 1 along with the deposition methods utilized. In situ transmittance measurements were taken as the potential was stepped from the neutral to the doped state of the polymer. Several trends are apparent when the results are presented on *xy* chromaticity diagrams. The first is the shape of the color track. It can be seen in Figure 3 for poly(3-methylthiophene) (**3**), as well as several other polymers (**4**, **10**−**12**), that as the potential is increased and the polymer is doped the *x* coordinate decreases and the *y* coordinate generally decreases, or decreases after an initial increase. In effect, the color track is following the outline of the spectral locus. Although the *xy* tracks for several polymers (**6**−**9**), including PProDOP-(CH$_3$)$_2$ (**8**) (Figure 4), do not appear to follow the spectral locus, the dominant wavelength of the transmitted light still does. This is due to the fact that if the projection from the white point through the measured point coincides with the purple line, the reverse projection is taken.[40] This effect is not surprising since, during the doping process, the absorbance of the $\pi-\pi^*$ transition is depleted at the expense of lower energy transitions. As a result, the absorbance maximum is shifted to longer wavelengths. Conversely, the complementary color, transmitted and seen by the observer, is shifted to shorter wavelengths as represented on the *xy* chromaticity diagram.

However, the cathodically coloring polymers PEDOT (**1**) and PProDOT-(CH$_3$)$_2$ (**2**) do not follow this rule (The *xy* track for PProDOT-(CH$_3$)$_2$ (**2**) (Figure 5) is representative of this class) since the *x* and *y* values increase as the polymer is doped. Note that here we define a cathodically coloring polymer as one that passes from a color neutral to a highly colored state upon charge neutrlization (i.e. reduction) of the p-doped form. In this case the $\pi-\pi^*$ transition is depleted at the expense of transitions outside the visible region. Therefore, the dominant wavelength of the color is the same throughout the doping process; the absorption decreases in intensity as represented by the decreasing saturation of the color as the *xy* coordinates change in a linear fashion. Similarly, as seen in Figure 6, the *xy* track for the cathodically coloring polymer PEDOP (**5**), which exhibits a deep red neutral state and a highly transmissive doped state, does not follow the spectral locus. In this instance, the direction of the linear *xy* change is altered due to the different initial color state.

In many polymers (**2**, **4**−**12**) (see Figures 4−6), a curling or tailing observed at high potentials in the color track represents a second trend. Examination of a spectroelectrochemical series for these polymers show that, with doping, the $\pi-\pi^*$ transition is depleted with the formation of two charge carrier (often termed bipolaron) transitions. At elevated doping levels the higher energy charge carrier transition loses intensity while the lower energy transition continues to increase in intensity. The tailing observed at high applied potential is caused by this bleaching of the higher energy charge carrier transition, with most of the absorbance found in the near-IR portion of the spectrum. Since there is very little absorbance in the visible region, the color changes observed are quite small as noted by the high concentration of points in the tail.

Although the *xy* chromaticity diagram is not a uniform color space, abrupt changes in color are found to correspond with large changes in the *xy* coordinates. This is best illustrated by PBTB-(OMe)$_2$ (**4**) (Figure 7). As the potential is switched from +0.93 to +0.98 V vs Ag/Ag$^+$, a large change in the *xy* coordinates occurs as the color abruptly changes from blue to green. Similar behavior is observed with LPEB (**12**).

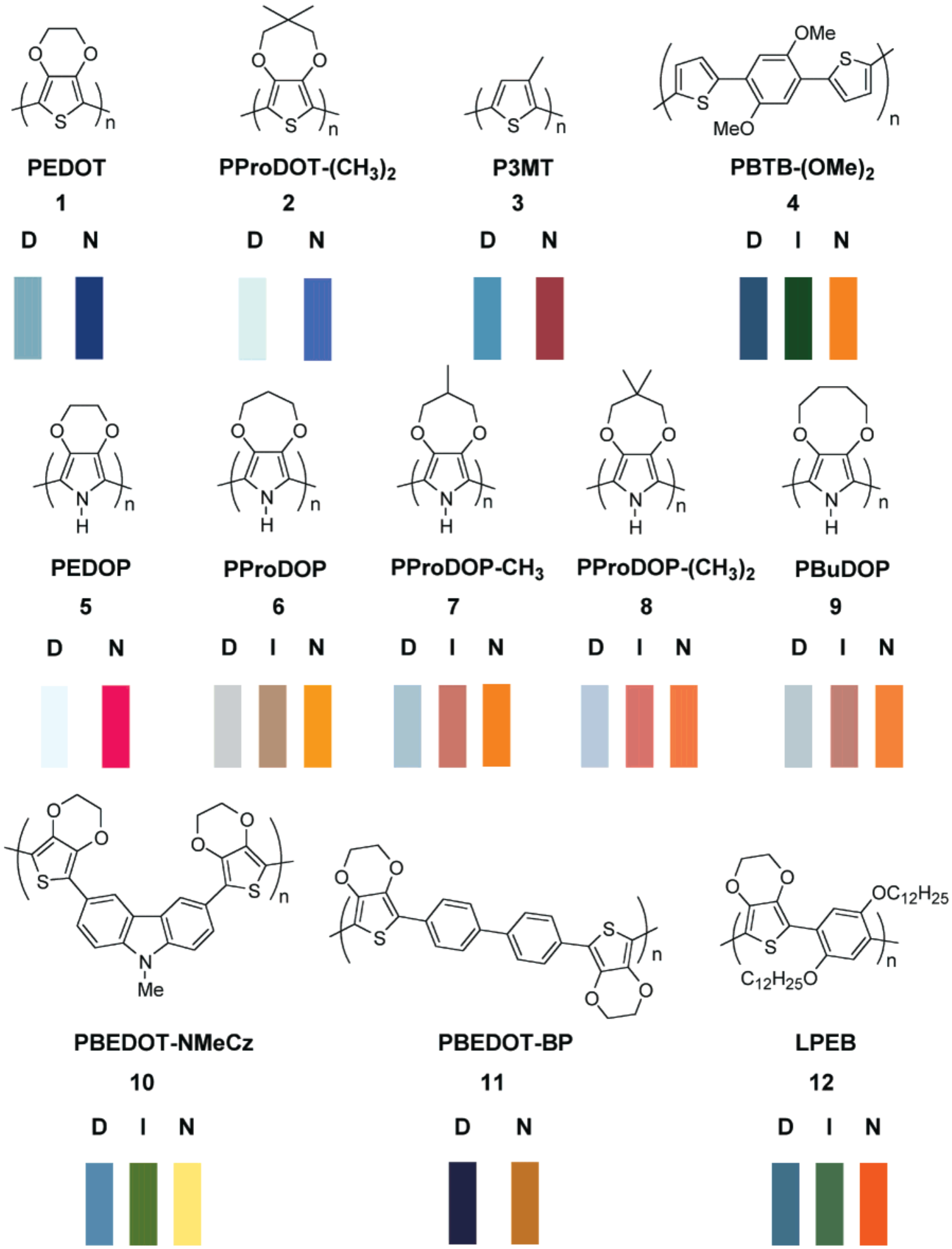

Figure 2. Chemical structures of all polymers characterized with colors corresponding to the doped state (D), neutral state (N), and intermediate state (I) if any.

Changes in the relative luminance (% *Y*) during doping also reveal trends and valuable information. In many polymers (**1**−**3**, **5**, **12**) the relative luminance is found to increase as the potential is increased. This strongly illustrated by PProDOT-$(CH_3)_2$ (**2**) (Figure 8a) where the relative luminance changes from 15% to about 75% with doping. As expected for cathodically coloring polymers, the relative luminance of the fully doped state is higher than that of the neutral state due to the depletion of the $\pi-\pi^*$ transition in the visible region at the expense of absorbances in the near-infrared.

However, some polymers do not follow this trend (**4**, **10**, **11**). For example, in PBEDOT-NMeCz (**10)** (Figure 8b), the luminance decreases as the potential is increased. PBEDOT-NMeCz has a relatively high band gap of 2.5 eV and, thus, much of the absorption in the neutral state is in the UV region of the spectrum. As

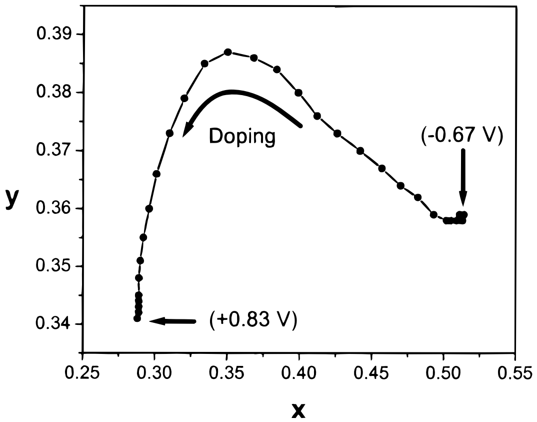

Figure 3. CIE 1931 *xy* chromaticity diagram for poly(3-methylthiophene) (**3**) as a function of applied potential. The potential was increased by 50 mV steps from the fully neutral state (−0.67 V vs Ag/Ag$^+$) to the fully doped state (+0.83 V vs Ag/Ag$^+$).

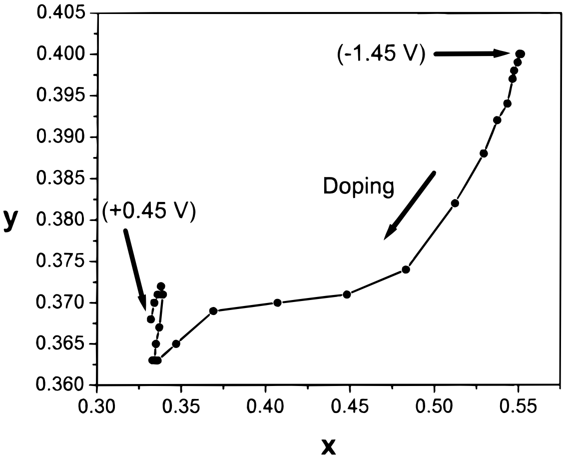

Figure 4. CIE 1931 *xy* chromaticity diagram for PProDOP-(CH$_3$)$_2$ (**8**) as a function of applied potential. The potential was increased by 50 mV steps from the fully neutral state (−1.45 V vs Ag/Ag$^+$) to the fully doped state (+0.45 V vs Ag/Ag$^+$).

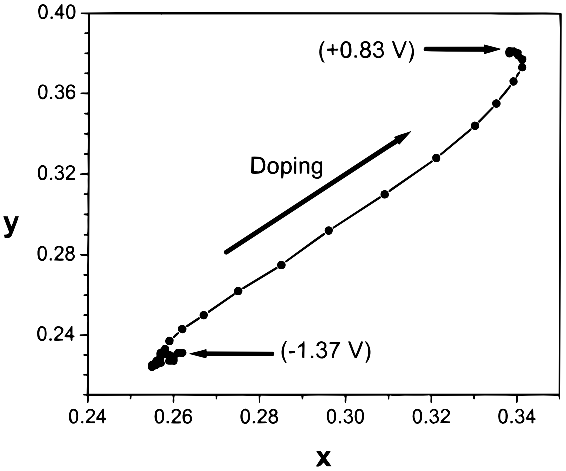

Figure 5. CIE 1931 *xy* chromaticity diagram for PProDOT-(CH$_3$)$_2$ (**2**) as a function of applied potential. The potential was increased by 50 mV steps from the fully neutral state (−1.37 V vs Ag/Ag$^+$) to the fully doped state (+0.83 V vs Ag/Ag$^+$).

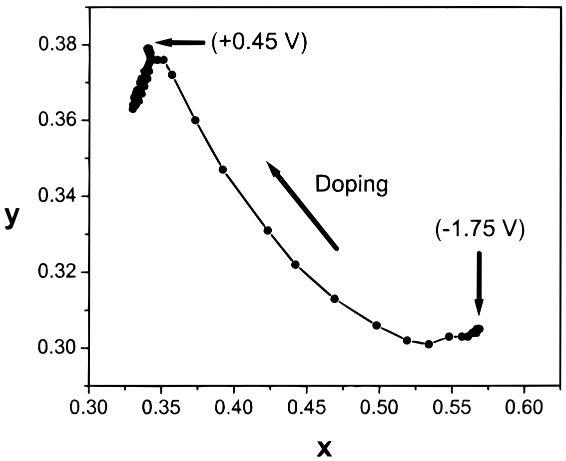

Figure 6. CIE 1931 *xy* chromaticity diagram for PEDOP (**5**) as a function of applied potential. The potential was increased by 50 mV steps from the fully neutral state (−1.75 V vs Ag/Ag$^+$) to the fully doped state (+0.45 V vs Ag/Ag$^+$).

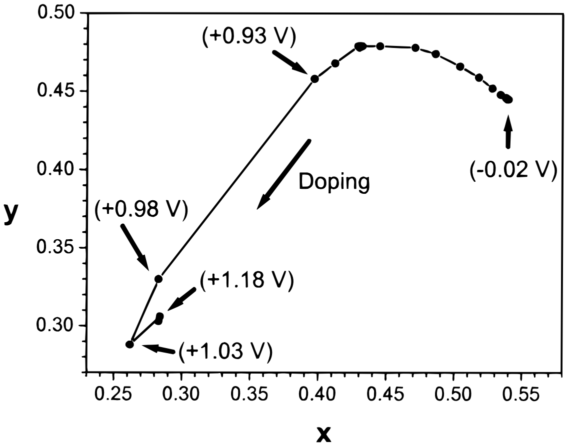

Figure 7. CIE 1931 *xy* chromaticity diagram for PBTB-(OCH$_3$)$_2$ (**4**) as a function of applied potential. The potential was increased by 50 mV steps from the fully neutral state (−0.02 V vs Ag/Ag$^+$) to the fully doped state (+1.03 V vs Ag/Ag$^+$).

the $\pi-\pi^*$ transition is depleted, two new absorption bands grow in.[46] As the doping process continues, the fully doped state is observed to be more absorbing across the visible region than the neutral state. This behavior is typical of other high band gap systems and anodically coloring polymers in general.[6]

A surprising behavior in the luminance is observed in polymers **6**−**9** and **12** which cannot be easily discerned from spectroelectrochemical results. As illustrated in Figure 8c for PProDOP−CH$_3$ (**7**), an intermediate dark state is observed which corresponds to the "well" in the luminance centered at −0.4 V vs. Ag/Ag$^+$. At intermediate potentials, an absorbance band grows in at the low energy end of the visible region before the band associated with the $\pi-\pi^*$ transition is completely bleached.[47] This leads to a state in which the polymer is absorbing light across much of the visible spectrum, corresponding to the dark state. At higher potentials this band along with the $\pi-\pi^*$ band are depleted and, as a result, the amount of light transmitted by the polymer is seen to increase.

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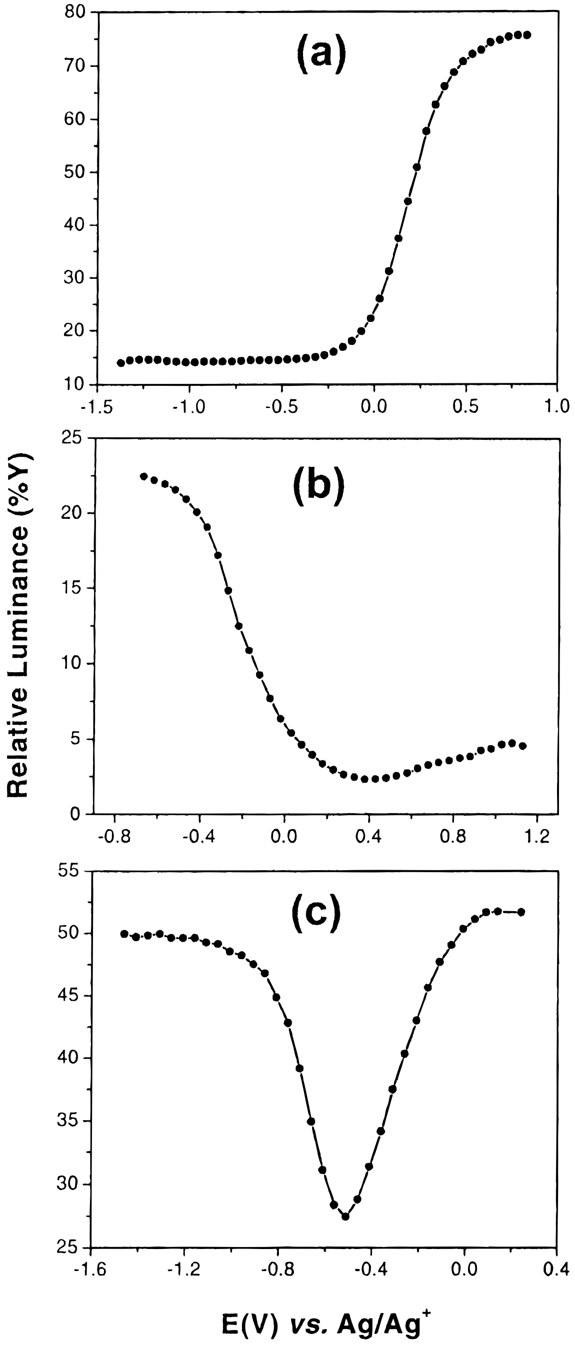

Figure 8. Relative luminance (% *Y*) vs applied potential (V) vs Ag/Ag$^+$: (a) PProDOT-$(CH_3)_2$ (**2**); (b) for PBEDOT-NMeCz (**10**); (c) PProDOP-CH_3 (**7**). For each polymer, the potential was increased by 50 mV steps from the fully neutral state to the fully doped state.

It is apparent that the relative luminance can offer a different perspective on a film's light transmittance relative to spectroelectrochemistry. First, relative luminance relates human eye sensitive information about transmittance over the entire visible region and the full range of applied potentials on a single curve. Such measurements are useful for electrochromics because a low value of luminance corresponds to an opaque material while a high value is characteristic of a highly transparent material. Second, the % *Y* vs potential relationship can be used for selecting the optimal color states exhibited by polymers. Third, % *Y* is more useful than %T for representing how bright the transmitted light is because *Y* is a tristimulus value and is defined in term of the color matching functions which incorporate human perception. As a result, luminance measurements are more useful than spectoelectrochemistry results for illustrating perceived changes in brightness. This is best illustrated by PProDOP-CH_3(**7**) (Figure 8c). The "well" in the luminance graph represents the point at which the polymer appears the darkest. This dark point is not readily apparent by examination of the corresponding spectroelectrochemistry.[47]

The above results delineate the benefit of using in situ colorimetric analysis for studying electrochromic processes in conjugated polymers. Both luminance and chromaticity coordinates provide valuable information that allows the observer to understand changes in a material's color. Since many advanced graphic software systems (e.g., Photoshop, Adobe Inc.) incorporate the *L*a*b** color space, a representation of the color seen is quite straightforward. Table 2 contains the *L*a*b** and *Yxy* coordinates for the doped and neutral states of each of the polymers studied. It is readily apparent that these polymers cover almost the entire CIE diagram if we consider both doped and neutral states. Fine-tuning of these color states can be attained via copolymerization, blend formation, or other methods of preparing multicomponent materials. The ability to design polymers with any desired color state is an asset when one considers the construction of dual-polymer electrochromic devices where the transmitted color is the sum of transmission through two separate films.[6,7] Below, we demonstrate how this method predicts the true color of these devices. In addition, should one desire to produce a precise color, specific polymer pairs can be selected.

Color Prediction in Electrochromic Devices. As a model, we have built a simple dual polymer device based on PBEDOT-NMeCz (**10**) and PBEDOT-BP (**11**) by examining the chromatic properties through both films simultaneously. These two polymers were chosen as they exhibit electrochromic properties in the same electrochemical potential window and their complementary doped and neutral states produce a device that is colored across the entire range of applied potentials. In accordance with color mixing theory, the point representing the predicted color of the device on the *xy* chromaticity diagram lies on the line connecting the points representing the two individual polymers as illustrated by Figure 9a. The predicted *xy* coordinates of the device were calculated based on a luminance weighted average of the measured *xy* chromaticity coordinates of each individual polymer. The device was found to switch from green (state 1) to brown (state 2) with a yellow intermediate (state 3). The results in state 1 (neutral poly(BEDOT-NMeCz)/fully doped poly(BEDOT-BP)) (Figure 9a) and state 2 (fully doped poly(BEDOT-NMeCz)/neutral poly(BEDOT-BP)) (Figure 9b) are seen to correlate with the expected results. The color differences (ΔE) between predicted and measured colors were calculated from the *L*a*b** coordinates using the CIELAB formula.[40,48] The calculated values of 6.6 and 6.7 for state 1 and state 2 respectively, indicate that the predicted and measured colors are not identical,

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Table 2. Lab and *Yxy* Coordinates of All Polymers Characterized in Both the Doped and Neutral States

polymer	*E* (V) vs Ag/Ag$^+$	% *Y*	*x*	*y*	*L*	*a*	*b*
PEDOT (**1**) doped	+0.83	35.9	0.314	0.368	66	−8	−8
PEDOT (**1**) neutral	−1.17	2.9	0.206	0.172	20	15	−43
PProDOT-(CH$_3$)$_2$ (**2**) doped	+0.83	75.5	0.338	0.380	90	−5	−1
PProDOT-(CH$_3$)$_2$ (**2**) neutral	−1.17	14.5	0.255	0.225	45	19	−49
P3MT (**3**) doped	+0.83	25.0	0.288	0.341	58	−8	17
P3MT (**3**) neutral	−0.67	10.4	0.515	0.356	38	38	19
PBTB−(OMe)$_2$ (**4**) doped	+1.08	6.9	0.283	0.303	32	1	−21
PBTB−(OMe)$_2$ (**4**) neutral	−0.02	34.5	0.540	0.445	65	35	89
PEDOP (**5**) doped	+0.45	53.0	0.340	0.379	96	−3	0
PEDOP (**5**) neutral	−1.75	11.0	0.569	0.305	50	77	20
PProDOP (**6**) doped	+0.25	68.5	0.346	0.380	83	0	1
PProDOP (**6**) neutral	−1.25	60.5	0.517	0.455	79	31	93
PProDOP−CH$_3$ (**7**) doped	+0.25	51.7	0.330	0.368	77	−3	−8
PProDOP−CH$_3$ (**7**) neutral	−1.45	49.9	0.545	0.425	76	47	85
PProDOP−(CH$_3$)$_2$ (**8**) doped	+0.25	58.4	0.336	0.371	81	−2	−5
PProDOP−(CH$_3$)$_2$ (**8**) neutral	−1.45	50.4	0.550	0.400	76	57	70
PBuDOP (**9**) doped	−0.05	49.9	0.331	0.369	78	−2	−3
PBuDOP (**9**) neutral	−1.25	44.0	0.539	0.412	72	47	69
PBEDOT-NMeCz (**10**) doped	+0.83	24.3	0.317	0.329	56	5	−21
PBEDOT-NMeCz (**10**) neutral	−0.67	76.9	0.420	0.475	90	−6	57
PBEDOT-BP (**11**) doped	+1.03	1.6	0.294	0.246	13	12	−18
PBEDOT-BP (**11**) neutral	−0.87	22.2	0.515	0.461	54	21	71
LPEB (**12**) doped	+1.03	11.7	0.286	0.331	41	−5	−19
LPEB (**12**) neutral	−0.17	29.8	0.612	0.376	61	70	85

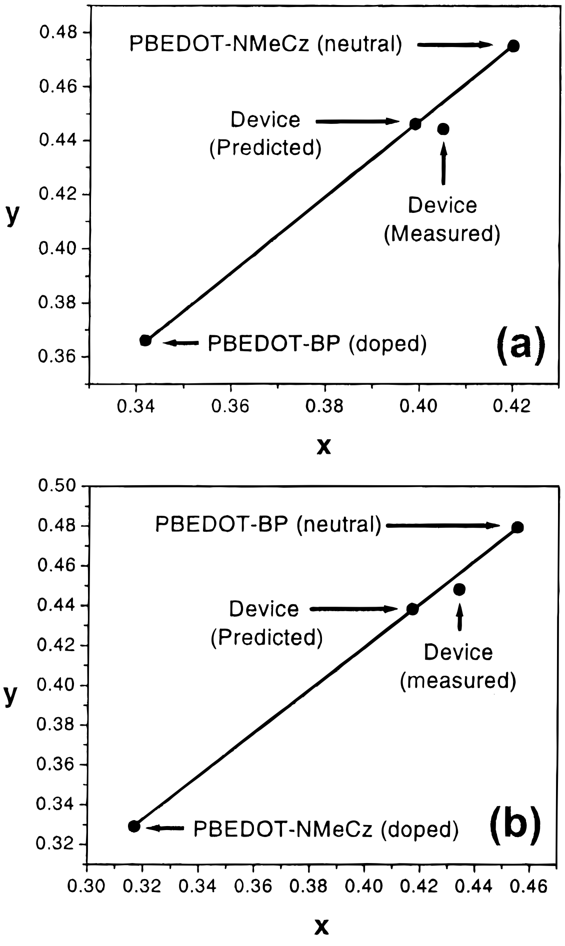

Figure 9. (a) Dual polymer electrochromic device in state 1 with PBEDOT-BP (**11**) in the blue doped state (+0.63 V vs Ag/Ag$^+$) and PBEDOT-NMeCz (**10**) in the yellow neutral state (−0.97 V vs Ag/Ag$^+$). (b) Dual polymer electrochromic device in state 2 with PBEDOT-BP (**11**) in the orange neutral state (−0.97 V vs Ag/Ag$^+$) and PBEDOT-NMeCz (**10**) in the blue doped state (+0.63 V vs Ag/Ag$^+$). The colors that were predicted for the device are labeled along with the colors actually measured.

Table 3. CIE 1931 *Yxy* Coordinates for the Dual Polymer Electrochromic Device[a]

	% *Y*	*x*	*y*	*L*	*a*	*b*
PBEDOT-BP (doped)	27.6	0.342	0.366	59	2	−7
PBEDOT-NMeCz (neutral)	76.9	0.420	0.475	90	−6	57
PBEDOT-BP (neutral)	64.5	0.455	0.479	84	6	71
PBEDOT-NMeCz (doped)	24.3	0.317	0.329	56	5	−21
device (state 1) measured	16.4	0.405	0.444	48	0	20
device (state 1) predicted	22.3	0.399	0.446	54	−2	22
device (state 2) measured	13.7	0.434	0.448	44	6	26
device (state 2) predicted	16.5	0.417	0.438	48	4	21

[a] Values are given for each individual polymer as well as the two states of the device.

although very similar. In each case, the device color is closer to the more transmissive polymer of the pair as can be seen in Table 3 as well as in parts a and b of Figure 9. This is expected, as the more transmissive polymer makes a larger contribution to the mixture. Because of the large effect of film thickness on color (namely on luminance), it is apparent that altering the thickness of the polymer films would allow a fine-tuning of the color in dual polymer electrochromic devices.

In potential applications, electrochromic devices with a specific color are desired. According to color mixing theory, many polymer pairs can be used to produce a given color. However, the practical realization of the device depends on other factors than just the colors that can be produced independently as a function of oxidation state. Among others, the electrochemical potential window certainly has the greatest impact on the choice of the polymers. In situ colorimetric analysis allows the prediction of the color produced by a dual device with a high degree of accuracy. The best way to realize a device with a precise color is therefore to choose the polymer pair that gives the closest predicted *xy* chromaticity coordinates to the electrochromic device color and then do a fine-tuning by adjusting the film thickness.

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Conclusion

Gaining the control of the color of dual electrochromic devices is not an easy task since many parameters are involved in the definition of color. Therefore, the trial and error method has historically been the most common technique in device construction. The in situ colorimetric analysis method discussed in this paper is a significant step in the direction of precise color control of polymer films and devices. In this paper, the electrochromic properties of 12 polymeric systems were analyzed by in situ colorimetry. By using the results given by in situ colorimetry analysis, a useful database can be built that can serve as a convenient tool for the realization of dual polymer electrochromic devices with specific controlled colors.

Experimental Section

General Data. All solvents were purchased from Fisher and distilled before use. All salts were purchased and used without further purification. ITO-coated glass slides (7 × 50 × 0.6 mm, 20 ohms per square) were purchased from Delta Technologies. 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.[39] The sample was 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 blank ITO in an electrolyte solution held in a standard quartz cuvette. The *Yxy* values of the standard illuminant were measured and converted to the X_n, Y_n, Z_n tristimulus values of the standard illuminant.[40] These tristimulus values were used with the calculated tristimulus values (X, Y, Z) of the sample for conversion to $L^*a^*b^*$ coordinates. A three-electrode cell was utilized, consisting of a silver wire pseudo reference electrode calibrated vs ferrocene, a Pt wire counter electrode, and an ITO working electrode. The potential was scanned in 50 mV steps. The potential was controlled by use of an EG&G Princeton Applied Research model 273 potentiostat/galvanostat under the control of Scribner and Associates Corrware II software.

Polymer Deposition and Characterization. The polymers were electrodeposited, except polymer **12** which was solution cast, as indicated in Table 1 using 10^{-2} M monomer in the indicated electrolyte. All films were deposited on ITO coated glass and cycled in monomer free electrolyte for CIE measurements. For additional information about the polymers see the references listed in Table 1.

Dual Polymer Electrochromic Device. For the device, PBEDOT-BP (**11**) and PBEDOT-NMeCz (**10**) were deposited on ITO electrodes to charge densities of 10mC/cm^2 each. In a 0.1 M solution of TBAP/CH$_3$CN in a cuvette with a silver wire pseudo-reference electrode, the PBEDOT-BP electrode and the PBEDOT-NMeCz electrode were controlled independently with a bipotentiostat through the use of a platinum wire counter electrode. As such, the potential was scanned in 50 mV steps from -1.17 to $+1.03$ V vs Ag/Ag$^+$, with respect to the PBEDOT-BP. The PBEDOT-BP was on the side of the device directly facing the colorimeter.

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