Organic Polymeric Electrochromic Devices: Polychromism with Very High Coloration Efficiency

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The electrochromic properties of electrodeposited poly(1,4-bis(2-[3′,4′-ethylenedioxy]thienyl)-2-methoxy-5-2′′-ethylhexyloxybenzene) (P(BEDOT-MEHB)), a material for polymer electrochromic displays, are reported in detail. While the polymer is transparent in the fully oxidized state, two absorption bands obtained in the visible region for the neutral and partially oxidized polymer are due to two different colors from the same material. Compared to other inorganic or organic electrochromic materials, the P(BEDOT-MEHB) films exhibited very high coloration efficiency values: as high as 680 cm^2/C at 535 nm and −360 cm^2/C at 760 nm. The films have the advantage of exhibiting cathodic and anodic coloration. The space created by the methoxy ethylhexyloxy benzene between EDOT units on the polymer backbone makes the injection/rejection of the negatively charged counterions inside/outside of the polymer easier, resulting in higher doping levels than PEDOT at the same optical density. Very well-defined electrochemistry, high level of stability to overoxidation and long-term switching, and the chromicity properties mentioned above make P(BEDOT-MEHB) an excellent candidate for electrochromic displays.

Introduction

Starting from the first report on electrochromism,[1] electrochromic materials have been largely studied for different technological applications, such as construction of mirrors,[2−4] displays,[5,6] windows,[7−10] and earth-tone chameleon materials.[11−13] Studies in electrochromic devices started with inorganic compounds such as tungsten trioxide (WO_3) and iridium dioxide (IrO_2).[14] Because of the different colors observed with these compounds while switching among their different redox states,[15,16] organic materials (viologens, metallophthalocyanines, and conducting polymers) have recently received much attention for electrochromic applications.[17] Conducting polymers have several advantages over inorganic compounds; these are outstanding coloration efficiency, fast switching ability,[18,19] multiple colors with the same material,[13,20,21] and fine-tuning of the band gap (and the color) through chemical structure modification.[22−25]

For commercial applications of electrochromics, stability, rapid response times, optical density changes, percent transmittance or luminance changes, low-power requirements, high efficient color changes, and ease of structural modification for color tuning are very important.[8,26] Substitution by electron-donating alkoxy substituents on the conjugated polymer's backbone produces a remarkable influence on its electrical, electrochemical, and optical properties.[27−31] Another bonus is

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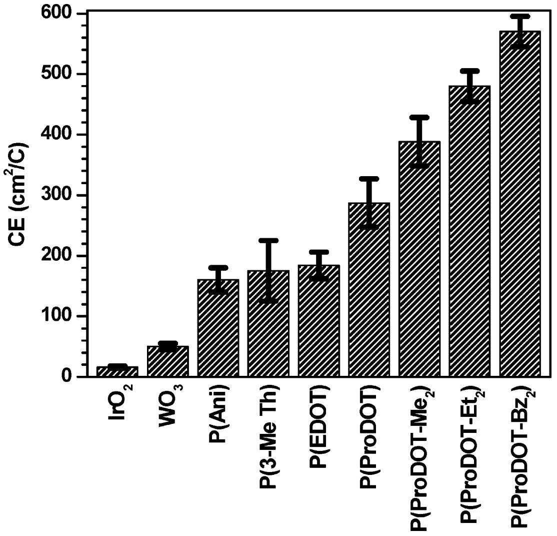

Figure 1. Coloration efficiency reported in the literature for inorganic compounds and conducting polymers. IrO_2, irridium dioxide; WO_3, tungsten trioxide; P(Ani), poly(aniline); P(3-Me Th), poly(3-methyl thiophene); P(EDOT), poly(3,4-ethylenedioxythiophene); P(ProDOT), poly(3,4-propylenedioxythiophene); P(ProDOT-Me_2), poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine), P(ProDOT-Et_2), poly(3,3-diethyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine); P(ProDOT-Bz_2), poly(3,3-dibenzyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine).

the improvement of the charge carriers' stability at different doping levels.[32] Electrochromic materials would be employed for the fabrication of very rapid, efficient displays and light modulators if they would exhibit sufficiently high coloration efficiency (CE), defined as the relationship between the injected/ejected charge as a function of electrode area and the change in optical density units.[15,33] The ideal device should exhibit a large change in transmittance with a small increase in charge, giving rise to large CE values. In comparing the CE values of the electrochromic materials to date, conducting polymers[26,34−37] are ahead of the inorganic solids,[14,38] as summarized in Figure 1. The latter shows that the use of conducting polymers as electrochromics causes an increase by 1 order of magnitude of CE values over the inorganic molecules. Note that the values reported in Figure 1 are the average of the reported values by different groups at different doping levels or under different conditions and the error bars show the maximum and minimum values. It should also be noted that these values could be improved by using dual electrochromic polymer devices.[18]

The stability of the polymer is another crucially important feature for practical use of materials for any purposes. We have recently reported the synthesis and stability of poly(1,4-bis(2-[3′,4′-ethylenedioxy]thienyl)-2-methoxy-5-2″-ethylhexyloxybenzene) (P(BEDOT-MEHB)) to both over-oxidation and extended switching. This polymer has a very well-defined electrochemistry and spectroelectrochemistry.[32] The P(BEDOT-MEHB) was also found to exhibit polychromism, an unusual phenomenon which demanded further exploration. Here we report a more detailed study of the electrochromic properties of this polymer, with emphasis on the elucidation of the polychromism.

Experimental Section

All chemicals were purchased from Aldrich Chemical. Propylene carbonate (PC) (99.7%, anhydrous) and acetonitrile (ACN) were distilled over calcium hydride before use. The 1,4-bis(2-[3′,4′-ethylenedioxy]thienyl)-2-methoxy-5-2″-ethylhexyloxybenzene (BEDOT-MEHB) monomer was synthesized according to the procedure reported before.[32]

Electropolymerization was carried out with a BAS 100B/W potentiostat, employing a platinum button (diameter, 1.6 mm; area, 0.02 cm^2) or ITO-coated glass slides as the working electrode, a platinum flag or wire as the counter electrode, and a silver wire or 0.01 M $Ag/AgNO_3$ (Ag/Ag^+) as the reference electrode. The electrolytes used were 0.1 M of $LiClO_4$ in PC or ACN. The electrodeposition was performed from a 0.01 M solution of the monomer in the electrolyte potentiodynamically at a scan rate of 20 mV/s or potentiostatically at the potential of 0.45 V vs Ag/Ag^+. Cyclic voltammetry was carried out using the same electrode setup using monomer-free electrolyte of 0.1 M $LiClO_4$ in PC or ACN.

Spectroelectrochemical data were recorded on a Shimadzu UV 3101PC UV−vis−NIR spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode was ITO-coated glass slides (7 × 50 × 0.6 mm, $R_s \leq 10\ \Omega/\square$, Delta Technologies Inc.), the counter electrode was a platinum wire, and a Ag wire was used as the pseudo-reference electrode. The pseudo-reference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc$^+$) in the electrolyte ($E_{1/2}$(Fc/Fc$^+$) = +0.140 V vs Ag wire and +0.075 V vs Ag/Ag^+ in 0.1 M $LiClO_4$/PC). The potentials are reported versus Ag/Ag^+. Polymer films for spectroelectrochemistry were prepared by potentiostatic deposition on ITO-coated glass slides. ITO-supported films were grown at 0.45 V vs Ag/Ag^+ in 0.1 M $LiClO_4$/PC containing 0.01 M of monomer.

The doping level (χ) of the polymer was calculated on the basis of the charges required for the polymerization (Q_p) and doping (Q_{ox}) of the film using the equation, $\chi = 2Q_{ox}/Q_p$.[29] The reason for multiplication by 2 is because of the two electrons transferred for each monomer in the generally accepted mechanism for the oxidative electropolymerization.[39] Optical density (ΔOD) at a specific wavelength (λ_{max}) was determined by using %T values in the oxidized and reduced states of the polymer according to the equation, $\Delta OD = \log(T_{ox}/T_{red})$ and the coloration efficiency (η) of the polymer was calculated by dividing the optical density of the injected/ejected charge as a function of electrode area (Q_d) using the equation $\eta = \Delta OD/Q_d$.[15,16,33,40]

Colorimetry measurements were obtained using a Minolta Chroma Meter CS-100A and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements.[41] As for spectroelectrochemistry, a three-electrode cell was employed. The potential was controlled by the same BAS 100B/W potentiostat. The sample was illuminated from

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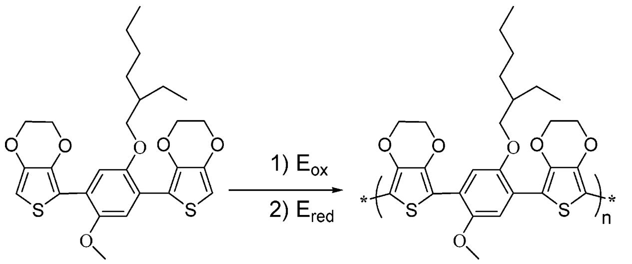
behind by a D50 (5000 K) light source in a light booth (Minolta GTI ColorMatcher) specially designed to exclude external light and to illuminate from behind. The color coordinates are expressed in the CIE 1931 Yxy color space where the *Y* value is a measure of the luminance in Cd/m^2. The relative luminance, expressed in %, was calculated by dividing the *Y* value measured on the sample by the Y_0 value corresponding to the background. Note that the relative luminance is frequently reported instead of the luminance because it gives a more meaningful value.[42]

A gel electrolyte based on PMMA (MW: 350.000) and $LiClO_4$ was plasticized with PC to form a highly transparent and conductive gel. ACN was also included as a high vapor pressure solvent to allow an easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN:PC:PMMA:$LiClO_4$ was 70:20:7:3. The gel electrolyte was used for construction of the polymer electrochromic device cell. A Fujifilm (FinePix 4500) digital camera was used to take photographs of the polymer electrochromic device cell at high resolution.

Results and Discussion

Electrochemistry. The oxidative electropolymerization of BEDOT-MEHB was carried out in propylene carbonate (PC) with 0.1 M $LiClO_4$ as electrolyte (Scheme 1). On the basis of BEDOT-MEHB's oxidation potential of +0.44 V vs Ag/Ag$^+$, polymer films were prepared on ITO-coated glass slides at a constant potential of +0.45 V vs Ag/Ag$^+$. These polymers were used for electrochemistry, spectroelectrochemistry, and colorimetric measurements. The polymer films were rinsed in monomer-free electrolyte solution and cycled potentiodynamically at least 10 times between −1.05 and +0.35 V vs Ag/Ag$^+$ to equilibrate the polymer before spectroelectrochemistry and colorimetric measurements. An example of the cyclic voltammetry of a thin P(BEDOT-MEHB) film (~120 nm) on an ITO-coated glass slide is given in Figure 2. The polymer film presents a very well-defined single redox process with an anodic peak potential of −0.15 V and a cathodic peak potential of −0.55 V, providing an $E_{1/2}$ of −0.35 V vs Ag/Ag$^+$ at a scan rate of 50 mV/s. It should be noted that this half-wave oxidation potential of the polymer on an ITO-coated glass slide is exactly the same value found for the polymer on a Pt button electrode vs the same reference electrode.[32] The films on the ITO-coated glass slides exhibited an extreme stability to long-term switching without losing their electroactivity. For ease of comparison, in Figures 2, 4, 5, and 6, the film used for cyclic voltammetry was also used to determine charge density, %Transmittance, optical density (ΔOD), coloration efficiency (CE), and doping levels.

Scheme 1



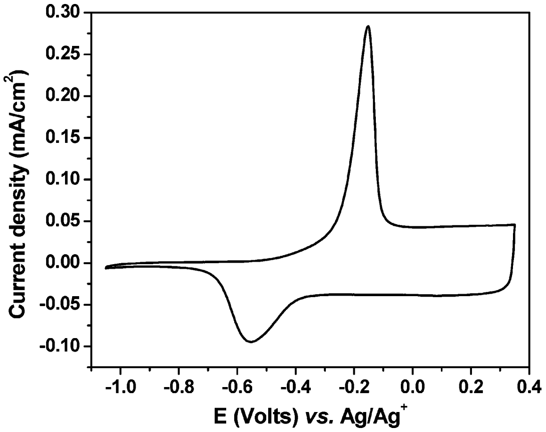


Figure 2. Cyclic voltammetry of 120-nm-thick P(BEDOT-MEHB) film on ITO-coated glass substrate in 0.1 M $LiClO_4$/ACN solution at a scan rate of 50 mV/s. The polymer film was deposited potentiostatically at 0.45 V vs Ag/Ag$^+$ from 0.1 M $LiClO_4$/PC solution containing 10^{-2} M monomer.

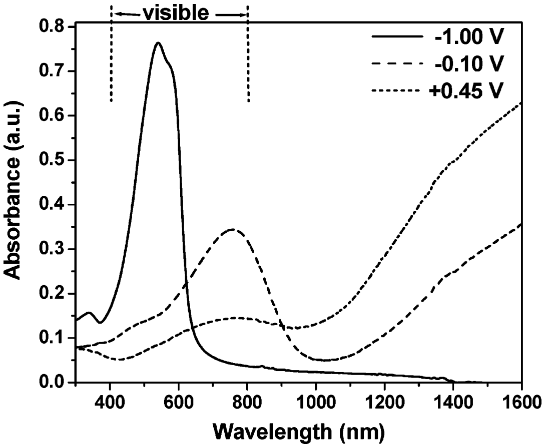


Figure 3. Spectroelectrochemistry of 150-nm-thick P(BEDOT-MEHB) film on ITO-coated glass substrate at three doping levels in 0.1 M $LiClO_4$/PC vs Ag/Ag$^+$: reduced state at −1.00 V, intermediate state at −0.10 V, and doped state at +0.45 V.

Spectroelectrochemistry. Thin films of P(BEDOT-MEHB) (~150 nm) were deposited on ITO-coated glass substrates using potentiostatic deposition at +0.45 V vs Ag/Ag$^+$ from a 0.01 M monomer solution in 0.1 M $LiClO_4$/PC. Figure 3 presents the spectroelectrochemistry of P(BEDOT-MEHB) at three different oxidation levels: reduced at −1.00 V, partially oxidized (intermediate doping level) at −0.10 V, and fully oxidized at 0.45 V vs Ag/Ag$^+$. The polymer film displays three noninterfering peaks at three different wavelengths, namely, 535 and 760 nm and a broad band in the near infrared (NIR), corresponding to the neutral, partially, and fully oxidized polymer, respectively. The electronic band gap calculated from the onset of the $\pi-\pi^*$ transition of the neutral polymer is found to be 1.95 eV. It should be noted that substitution of EDOT by insertion of a methoxy ethylhexyloxy benzene between two EDOT monomers results in an increase in the band gap of the polymer from 1.6 eV ($\lambda_{max} = 620$ nm) for regular PEDOT to 1.95 eV ($\lambda_{max} = 535$ nm) for P(BEDOT-MEHB). This substitution also gives stability to the species at the intermediate doping levels with a new band at 760 nm in the visible region. So the same polymer can produce two highly saturated colors in two oxidation states and a transmissive polymer in another state. While the

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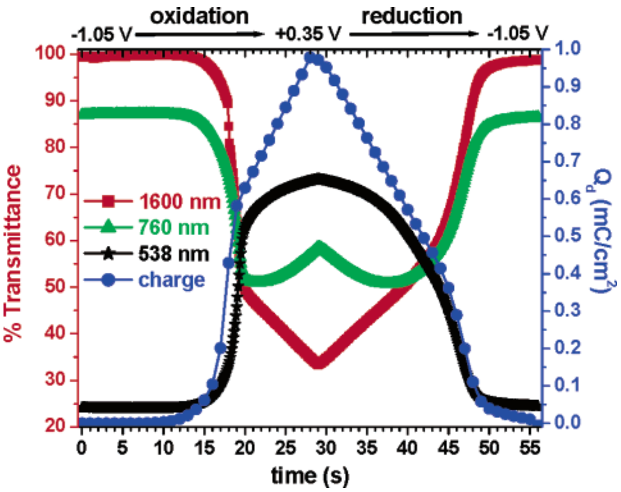

Figure 4. % Transmittance of 120-nm-thick P(BEDOT-MEHB) film on ITO-coated glass slides at three wavelengths: 535 nm (black line), 760 nm (green line), and 1600 nm (red line) during oxidation and reduction of the polymer film as a function of time and the charge stored by the polymer (blue line).

neutral polymer (at −1.00 V vs Ag/Ag$^+$) absorbs in the center of the visible region (535 nm), giving a very saturated purple-red color, low-energy charge carriers at the intermediate doping levels (−0.10 V vs Ag/Ag$^+$) also absorb at the edge of the visible region (760 nm), giving a deep-blue-colored polymer.

As the applied potential was increased, the absorption decreased in both the $\pi-\pi^*$ transition (535 nm) and mid-energy intergap transition (radical cations, 760 nm), producing a polymer film transparent in the visible and an extensive absorption in the NIR at the potential of +0.45 V vs Ag/Ag$^+$. It should be emphasized that coloring at the cathodic and anodic sides of the half-wave oxidation potential of a conducting polymer is not very common[43] and appears to be *sui-generis* for this particular polymer.

Coloration Efficiency. The charge accumulated by a polymer film is directly related to the concentration of the species created in the polymer backbone. Consequently, it is very informative to measure the charge passed at every step of oxidation or reduction with the absorption change at a specific wavelength. During the cyclic voltammetry measurement of a 120-nm-thick P(BEDOT-MEHB) film on an ITO-coated glass slide (Figure 2), the change in percent transmittance (%T) of the film at the specific wavelengths (535, 760, and 1600 nm) was followed spectrophotometrically. The charge (Q_d) injected/rejected during the CV was calculated by integrating the current density passing through the system when the polymer film was cycled between −1.05 and +0.35 V vs Ag/Ag$^+$ (scan rate, 50 mV/s). Figure 4 depicts the change in the %T of the P(BEDOT-MEHB) film on an ITO-coated glass slide at 535, 760, and 1600 nm as a function of charge injection and rejection into and from the polymer. The oxidation and reduction processes of the polymer can be divided into four steps of charge storage and transmittance. In the first step of oxidation, between 0 and 10 s (where the applied potential E_{app} was increased from −1.05 to −0.55 V vs Ag/Ag$^+$), no charge was accumulated. The %T of the polymer film did not change at the three wavelengths mentioned because the polymer film was in its neutral, insulating form. In the second step (10−15 s, E_{app} = −0.55 to −0.30 V vs Ag/Ag$^+$), a gradual increase was observed in both charge density and %T, where the polymer film started to oxidize. A very sharp change in the charge density and %T occurred between 15 and 19 s (E_{app}= −0.30 to −0.10 V vs Ag/Ag$^+$) as polaronic sites in the polymer backbone were created to afford a polymer film that was highly oxidized and highly conductive. In this interval, the doping level (χ) of the polymer, which is related to conductivity, had increased from 0.025 to 0.23 (see Figure 6). Very rapid changes in the optical properties of the polymer were also observed in this time interval. For example, the %T of the polymer increased from 24% to 64% at 535 nm and decreased from 87% to 51% at 760 nm as well as from 100% to 51% at 1600 nm. In Figure 6, the main change in the recorded optical density of the polymer in a time interval from 15 to 19 s (4 s) is misleading because the switching time is dependent on scan rate. For example, as the potential was stepped between −1.0 and +0.5 V, the polymer film switched between fully oxidized and fully reduced states in 0.5 s. In the last oxidation step between 19 and 28 s (E_{app}= −0.10 to +0.35 V vs Ag/Ag$^+$), the rate of charge accumulation in the polymer film decreased, though the doping level still increased substantially (from 0.22 to 0.39, Figure 6, filled squares). At the same time, the change in optical properties decreased (Figure 6, filled circles and triangles). In this range, the charge density increased from 0.58 to 0.98 mC/cm^2, providing a total change in the %T (%ΔT) of the polymer film of 10%, 8%, and 18% at 535, 760, and 1600 nm, respectively. Injection of this much charge did not result in a large change in the optical properties of the polymer film in the visible region but did so in the NIR, implying that the charge accumulated in the polymer film was mainly in the form of bipolarons (dications). Note that the charge and the applied potential required for the generation of polarons and bipolarons depends on the thickness and medium used to switch the polymer film. Using different polymer thicknesses and switching them in different media may result in a small change in the concentration of the species created or annihilated during oxidation (compare Figures 3 and 4). For example, in Figure 3, the %ΔT in two different oxidation levels (−0.10 and +0.45 V vs Ag/Ag$^+$) are 9%, 27%, and 21% at 535, 760, and 1600 nm, respectively, meaning that mostly polarons are converted to bipolarons. These data are slightly different in Figure 4, where it appears as though both the neutral polymer and the polarons were converted to bipolarons. The reduction process appears as the mirror image of the oxidation process, with smoother transitions between potential intervals.

The optical density (ΔOD) at a specific wavelength (λ_{max}) was determined by using %T values of the electrochemically oxidized and reduced films, using the equation $\Delta OD = \log(T_{ox}/T_{red})$. The coloration efficiency (η) of the polymer was calculated by dividing the optical density at an injected charge as a function of electrode area (Q_d), using the equation $\eta = \Delta OD/Q_d$. The change in optical density at three wavelengths (535, 760, and

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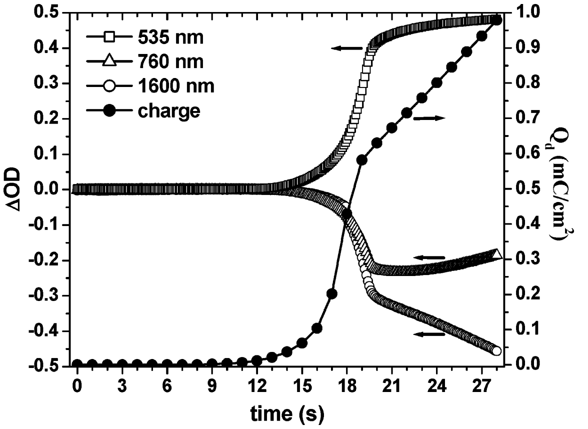

Figure 5. Optical density of 120-nm-thick P(BEDOT-MEHB) film on ITO-coated glass substrates at three wavelengths: 535 nm (□), 760 nm (△), and 1600 nm (○) nm during oxidation of the polymer film as a function of time and charge density (●).

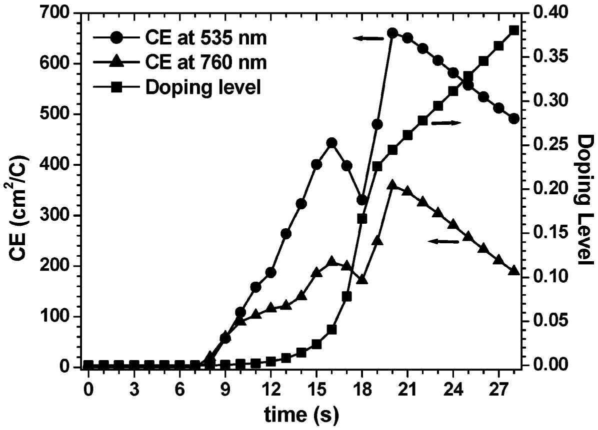

Figure 6. Coloration efficiency of P(BEDOT-MEHB) film on ITO-coated glass substrate at two wavelengths in the visible region: 535 nm (●) and 760 nm (▲), during oxidation of the polymer film as a function of time and doping level (■).

1600 nm) and coloration efficiency at the wavelengths in the visible region (535 and 760 nm) as a function of time are given in Figures 5 and 6, respectively. The charge accumulated in the polymer film and the doping levels are also given as a function of time to help in the comparison. To better understand the improvement in coloration efficiency in going from PEDOT to P(BEDOT-MEHB), it is instructive to compare the optical density reported here with PEDOT, reported by the Reynolds group.[26] While PEDOT films store about 2.13 mC/cm^2 of charge to attain an optical density value of 0.44, the same optical density can be obtained by charge of only 0.63 mC/cm^2 in a P(BEDOT-MEHB) film. This charge is 3.4 times lower than that of PEDOT, implying that the coloration efficiency should be at least 3.4 times higher than that in PEDOT. On the other hand, while the doping level of PEDOT reaches 0.15 at the same stage of optical density, P(BEDOT-MEHB) exhibits a much higher doping level of 0.25. Also a charge of 3.64 mC/cm^2 was required to reach a doping level of 0.25 for PEDOT[26] and a 5.8 times lower charge (0.63 mC/cm^2) was required to reach the same doping level for the P(BEDOT-MEHB). This difference may stem from the space created between two EDOT units by insertion of the methoxy and ethylhexyloxy benzene on the polymer backbone, which is expected to allow easier injection/rejection of the dopant ions inside/outside of the polymer. This should give rise to higher doping levels at lower oxidation potentials compared to PEDOT. Another consequence of the same substituents is a blue shift of the neutral polymer's $\pi-\pi^*$, compared to PEDOT, as well as the appearance of a stable absorption band of the polarons at the edge of the visible region (760 nm) so that a multicolored polymer was obtained. An optical density of −0.23 was obtained at 760 nm when a charge of 0.63 mC/cm^2 was injected into the polymer, affording a maximum coloration efficiency of −365 cm^2/C at this wavelength (Figure 5). Clearly, the coloration efficiency obtained from the same polymer at another wavelength is much higher than the coloration efficiency of inorganic compounds and most of the conducting polymers reported (see Figure 1). Since the charge injected into the polymer was used to create bipolarons at the time interval of 20−28 s, the optical density of the polymer starts to stabilize at 535 nm and decreases at 760 nm while maintaining a considerable increase at 1600 nm. As the doping level reaches 0.38 in the fully oxidized state, optical densities of 0.480, −0.185, and −0.455 are obtained at 535, 760, and 1600 nm, respectively. It should be emphasized that there are two intervals where the coloration efficiency of the polymer decreases. The first decrease occurred at the time interval of 16−18 s due to a rapid increase in the charge density, while the second decrease occurred at the time interval of 20−28 s. A possible interpretation is that the polymer reaches essentially its full contrast and the charge injected does not affect the optical density as dramatically after 20 s as before. Hence, the coloration efficiency values of the polymer decrease to 493 and 190 cm^2/C at 535 and 760 nm, respectively, in the fully oxidized state.

Colorimetry. A polymer's color is one of the most important properties for its application in display devices and needs to be defined precisely. Since P(BEDOT-MEHB) exhibits interesting electrochemical and optical properties, we studied the in situ colorimetric analysis of P(BEDOT-MEHB) by colorimetry and the results are expressed in the CIE 1931 *Yxy* and CIE 1976 *L*a*b** color spaces as recommended by the "Commission Internationale de l'Eclairage" (CIE).[44] For colorimetric analysis, 0.2-μm-thick P(BEDOT-MEHB) films on ITO-coated glass slides were prepared from 10^{-2} M monomer solutions in 0.1 M $LiClO_4$/PC. Measurements were conducted in a monomer-free electrolyte solution of 0.1 M $LiClO_4$/ACN. The applied potential dependence of the colors observed, %*Y*, and *L*a*b** color spaces for the polymer films are summarized in Table 1. Upon oxidation, the polymer film changed color from deep purple-red to pale blue through a darker blue intermediate. Luminance, which is a coordinate in the *Yxy* color space, represents the brightness of a color as seen by the human eye. It is also very informative since, with only one value, it provides information about the perceived transparency of a sample over the entire visible range. It should be noted that %*Y* is different from %*T* because it takes into account the light sensitivity of the human eye, which is not constant over the entire visible range.[45]

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[44] CIE. *Colorimetry* (Official Recommandations of the International Commision on Illumination); CIE Publication No. 15; CIE: Paris, 1971.

[45] Nassau, K. *Color for Science, Art and Technology*; Elsevier: Amsterdam, 1998.

Table 1. Potential-Dependent CIE 1931 *Yxy* and CIE 1976 *L*a*b Color Spaces for P(BEDOT-MEHB)**

E (V) vs Ag/Ag$^+$	Y (%)	L	a	b	color
−1.00	11.0	40	43	−8	deep red-purple
−0.80	10.9	39	45	−8	
−0.60	10.8	39	45	−9	
−0.50	10.8	39	46	−10	
−0.45	11.0	39	46	−12	
−0.40	11.5	40	47	−20	purple-blue
−0.35	11.8	40	47	−28	
−0.30	12.3	41	47	−30	
−0.25	15.6	46	33	−35	blue
−0.20	21.1	53	−9	−40	
−0.15	42.2	71	3	−14	gray-blue
−0.10	47.9	75	−1	−11	
−0.05	51.9	77	−4	−10	
0.00	56.1	80	−6	−10	pale blue
0.05	58.3	81	−6	−11	
0.10	60.0	82	−6	−12	
0.15	61.1	82	−6	−13	
0.20	62.0	83	−2	−12	
0.30	63.8	84	5	−11	
0.40	65.8	85	6	−12	

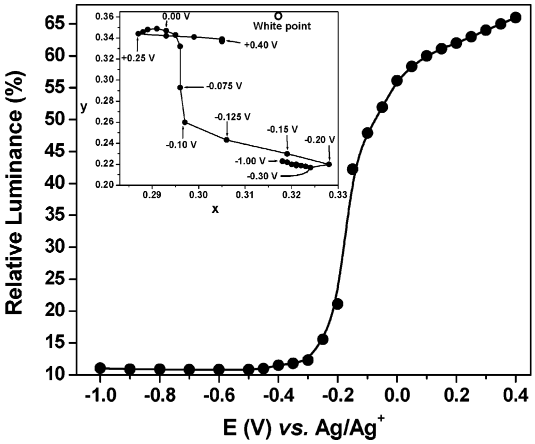

Figure 7. Relative luminance of P(BEDOT-MEHB) film on ITO-coated glass slides as a function of the applied potential vs Ag/Ag$^+$. Colorimetry (x−y diagram) of P(BEDOT-MEHB) film on ITO-coated glass slides (inset figure).

The color track of the P(BEDOT-MEHB) film in the CIE 1931 *Yxy* color space and relative luminance (%Y) as a function of applied potential is shown in Figure 7. Clearly, between −1.00 and −0.30 V vs Ag/Ag$^+$, the xy coordinates are very close to each other, signifying no visible change in the purple-red polymer color. The x and y coordinates are 0.318 and 0.223 at −1.00 V as well as 0.324 and 0.217, respectively, at −0.30 V. The relative luminance of the polymer film in this range of applied potential is also very stable at its darkest state about 11%. Starting from an applied potential of −0.30 V, initial oxidation results in abrupt changes in color so that large changes in the xy coordinates are observed. As the potential is stepped up to −0.10 V, the film turns a more transparent blue color, corresponding to the *Yxy* coordinates: $x = 0.297$, $y = 0.260$, and $Y = 48\%$. In the inset of Figure 7, as one proceeds in x values from 0.33 to 0.29 (from right to left of Figure 7 inset), where blue is more saturated between reduced and oxidized states, a new blue color is observed at the corner of the kink labeled −0.10 V. As the potential increases, the luminance increases and a curling is observed in xy coordinates at higher oxidation levels. This could be due to the depletion of the π−π^* transition at 535 nm and the polarons at 760 nm at the expense of the increase in absorption of bipolarons in the NIR region. As the intensity of the absorption decreases in the visible region (bleaching) upon doping, the xy coordinates move closer to the white point, making the polymer film more transparent and resulting in a relative luminance of 66%. The total change in the relative luminance is 55% between fully reduced and oxidized states. The x and y coordinates of the film in the color track in the heavily doped state are 0.305 and 0.337, respectively (+0.40 V, Figure 7 inset).

Figure 8. Colors of a sandwich-type P(BEDOT-MEHB) EC cell at three oxidation levels: (A) neutral, (B) intermediate, and (C) oxidized states.

Polymer Electrochromic Cell. A 0.3-μm-thick P(BEDOT-MEHB) film was prepared on an ITO-coated glass slide at a constant potential of +0.45 V vs Ag/Ag$^+$ from a 0.01 M monomer solution in 0.1 M $LiClO_4$/PC. After rinsing in a monomer-free electrolyte solution, the polymer film was cycled between its reduced and oxidized states 10 times, followed by covering with a gel electrolyte and sandwiched with another blank ITO-coated glass slide. The polymer electrochromic cell was then allowed to dry for 24 h at room temperature in a laboratory atmosphere. Switching tests were done in laboratory air using a two-electrode potentiostat (reference and counter electrode shorted together). The letters “UCLA” (purple-red) and “EMI” (blue) printed on white paper were used as background. Figure 8 shows photographs of the P(BEDOT-MEHB) ECD cell at three different oxidation levels. Since the polymer and the UCLA letters have identical colors when the polymer electrochromic cell was held in the neutral state by applying a potential of −2.85 V, it is impossible to read “UCLA” located at the left part of the background (Figure 8A). As the applied potential was increased to 0.0 V, the polymer in the cell was partially oxidized, changing its color from purple-red to blue, so that “UCLA” appeared (Figure 8B). In the fully oxidized state at 1.8 V, the polymer is highly transparent and all the background letters can be read easily (Figure 8C). Since the absorption at 760 nm was not strong enough to obtain a very saturated blue color, we were unable to “erase” the blue-colored letters of EMI completely. Colorimetric analysis of the polymer electrochromic cell gave $L^*a^*b^*$ coordinates of 52, 59, −2 in the reduced, 64, 9, −13, in the intermediate, and 90, −1, −7 in the oxidized states. It should be noted that the colors corresponding to these values are lighter than the colors represented in Figure 8 because the illumination of the device is from behind with an intense light source during the colorimetric measurement.

Conclusions

In conclusion, the insertion of a methoxy ethylhexyloxy benzene ring between two EDOT monomers results in a decrease in wavelength of the neutral polymer's $\pi-\pi^*$ transition. As a result, another absorption band of stable polarons arises at the edge of the visible region, producing both a cathodically and an anodically colored polymer. The P(BEDOT-MEHB) films exhibited a coloration efficiency value as high as 680 cm^2/C at 535 nm and -360 cm^2/C at 760 nm. The coloration efficiency at 535 nm (with an additional anodic coloration at 760 nm) is almost 4 times higher than PEDOT and much higher than any other system reported to date. Moreover, the steric bulk of the methoxy ethylhexyloxy benzene between EDOT units on the polymer backbone improves the facility of counterions injection/rejection, generating higher doping levels than PEDOT at the same optical densities. As a material, P(BEDOT-MEHB) is an excellent candidate for electrochromic displays, exhibiting very well-defined electrochemistry, high robustness to overoxidation, and long-term switching stability.[32] Other features are transparency in the fully oxidized state and high contrast ratio and multicoloration with very high coloration efficiencies at two different wavelengths in the visible region.

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