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Black to Transmissive Switching in a Pseudo Three-Electrode Electrochromic Device

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We introduce the first π-conjugated polymer-based, black-to-transmissive and multicolored switching electrochromic device (ECD) constructed in a Pseudo 3-Electrode Electrochromic Device (P3-ECD) architecture. In this ECD, the non-electrochromic, yet electroactive, polymer poly(3,4-propylenedioxypyrrole-*N*-propionitrile) (PProDOP-N-EtCN) serves as a counter electrode material. This transmissive polymer helps eliminate the contrast limitations seen in dual polymer ECDs that use combinations of anodically and cathodically coloring polymers. The P3-ECD adds colors by transmitting light through two independently controlled working electrodes (coated with two different electrochromic polymer films) and two counter electrodes (coated with PProDOP-N-EtCN) stacked together with a gel electrolyte. The two cathodically coloring EC polymers that were used in this work are, a diester-substituted poly(3,4-propylenedioxythiophene) (PProDOT-$(CH_2CO_2C_{12}H_{25})_2$) for the first one, namely PProDOT-ester, and a donor−acceptor analogue, namely PProDOT-BTD, which consists of a specific alternation of donor and acceptor building units spanning the electron-rich 3,4-ethylenedioxythiophene (EDOT), 2-ethylhexyloxy-substituted 3,4-propylenedioxythiophene ProDOT-$(CH_2O(2\text{-EtHx}))_2$ and the electron-deficient 2,1,3-benzothiadiazole (BTD). The PProDOT-ester switches from a deep purple ($L^* = 41$ $a^* = 22$ $b^* = -48$) to a highly transmissive gray/blue ($L^* = 87$ $a^* = -2$ $b^* = -7$), while the PProDOT-BTD switches from a deep green ($L^* = 60, a^* = -23, b^* = 12$) to transmissive sky blue ($L^* = 84, a^* = -4, b^* = -6$). Utilizing PProDOT-ester and PProDOT-BTD in their neutral form in the P3-ECD yields a deep blue-black with color coordinates of $L^* = 26$,$a^* = -3, b^* = -17$ switching to a transmissive state with color coordinates of $L^* = 75, a^* = -7, b^* = -7$. The device has a high Michelson contrast of 0.8 (which can range from 0 to 1). Separate potential control over the electrodes allows color mixing of the polymers in intermediate oxidation states in the P3-ECD. As such, a full palette of colors is accessible through proper choice of EC materials as desired for the construction of multicolored information displays, and in the case of black-to-transmissive electronic paper.

Introduction

Electrochromism consists in the formation of new optical transitions in an electroactive species subjected to reversible electrochemical oxidation/reduction reaction.[1−3] There are three general classes of electrochromic materials; inorganic materials such as transition metal oxides and Prussian Blue, molecular electrochromes such as viologens, and conjugated polymers.[3−8] The most widespread applications of electrochromic materials include rear-view mirrors,[4] protective eyewear,[4] displays,[9] smart windows,[1] optical shutters,[7] optical data storage,[1] and electronic paper.[10] Conjugated polymers are finding increasing use in electrochromic applications because of their cathodic, anodic and multicolor control, ease in processability, flexibility, rapid redox switching, high optical contrast, and long-term stability.

Conjugated polymers provide the ability to access various electrochromic states in both the doped and neutral forms by controlling the band gap through structural modification of the pendant groups or the conjugated backbone.[11,12] The range of colors obtained from conjugated polymers based on thiophene and pyrrole

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moieties, such as the poly(3,4-alkylenedioxythiophene)s (PXDOTs) and poly(3,4-alkylenedioxypyrrole)s (PXDOPs), spans the entire visible spectrum and extends into the UV and NIR regions.[9] It has been shown that the electrochromic contrast of these two polymer families can be enhanced by increasing the size of the alkylenedioxy ring, or the bulkiness of the substituent attached to the ring.[13−15] In the first systematic study of the PXDOTs, our group reported on high optical contrasts and fast switching times for the dialkyl-substituted (along the alkylene bridge) PProDOTs compared to the parent unsubstituted PProDOT.[16] Typically, a strong NIR absorption overlapping into the visible region appears as the polymer is doped. It is the attenuated overlap of this NIR absorption as it crosses through the visible region that causes the higher transmissivity for the PProDOT derivatives. For example, ProDOT-Me_2, dimethyl-substituted on the central carbon of the propylene bridge, was shown to exhibit a high optical contrast of 78% ($\Delta\%T$) at 578 nm.[14] More highly substituted PXDOT derivatives, prepared by both electrochemical and solution polymerization methods, exhibit high optical contrasts, switching from deep red-purple to highly transmissive sky blue where the human eye is highly sensitive, and exhibit fast switching times because of their more open morphology.[17−19,21,22] Considering their commercial viability as solution-processable electrochromes with a broad set of accessible color states, these polymers have been assigned the SprayDOT trademark. SprayDOTs have the advantage of being soluble in their reduced form in several organic solvents, allowing the deposition of high-quality films by spraying or spin-coating and can be potentially incorporated in ink-type formulations.[12,18,24] Of these polymers, PProDOT-$(CH_2OEtHx)_2$ exhibits an especially useful spray-processability along with a high transmittance contrast of 80% ($\Delta\%T$) at 581 nm and a luminance contrast of 56% ($\Delta\%Y$) as it switches from magenta to clear.[18,23]

One major focus in developing processable, high contrast EC polymers has been to establish a full color palette for use in displays. While red and blue polymers becoming highly transmissive upon oxidation have been frequently described,[3] green polymers that absorb both the red and blue regions of the electromagnetic spectrum had represented a challenge only recently overcome. The first electrochemically stable green polymer was reported by Sonmez et al.,[25] and was shown to switch to a transmisive brown hue upon doping.[26,27] Our group has reported on a set of green to transmissive switching polymers and one of them, PProDOT-BTD, was used for the electrochromic applications in this manuscript (although with 2-ethylhexyl solubilizing side-chains instead of the linear octyl).[30] The polymer was composed of alternating electron-rich EDOT, 2-ethylhexyloxy-substituted 3,4-propylenedioxythiophene ProDOT-$(CH_2O(2\text{-}EtHx))_2$, and electron-deficient 2,1,3-benzothiadiazole (BTD) building units. In parallel, Toppare et al. reported on both electrochemically, along with chemically prepared and solution processable, green polymer, PDOPEQ, with a highly transmissive oxidized state.[28,29]

Ultimately, in the context of color control, it would prove useful to have a material switching between two extreme optical states such as opaque black and transmissive as is possible with some inorganic materials.[1] As far as polymer electrochromes are concerned, we note that the synthesis of a black-to-clear switching and processable conjugated material was recently reported by Beaujuge et al.[32] In addition to designing new polymers, new colors can be achieved by adding the colors of component films. Toward this end, we reported on a dual-polymer electrochromic film characterization method as an analytical tool further allowing color mixing.[33] Color mixing theory (the lever rule) states that when two colors are mixed, the xy-coordinates of the resulting color lies on the line joining the two original chromaticity coordinates.[27,31] This has been exploited in dual polymer absorptive/transmissive ECDs, used for color mixing.[25] The dual electrochromic device design involves the use of a second electrochromic material on the counter electrode to balance the reaction of the working electrode, and prevent early degradation of the functional material. Importantly, the electrochromic materials are required to have complementary optical properties; one anodically coloring and the other cathodically coloring.[23,34] As reported by Otero and Padilla, the contrast achieved in

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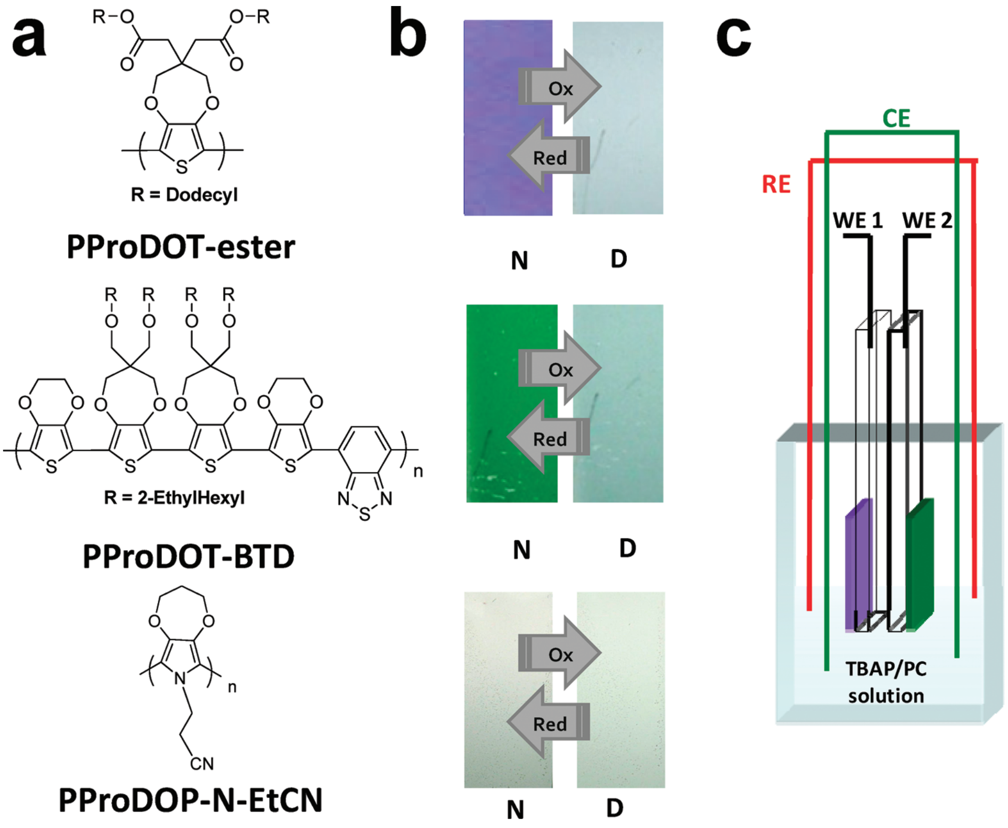

Figure 1. (a) Repeat unit structures of the polymers used in the dual-polymer electrochromic method and P3-ECD, (b) photographs of their neutral (N) and oxidatively doped (D) states. PProDOT-ester and PProDOT-BTD were sprayed from toluene solution and PProDOP-*N*-EtCN was electrodeposited by potential scanning (10 scans, 50 mV/s, −0.30 V to +0.80 V vs Fc/Fc$^+$), and (c) schematic of the dual-polymer electrochromic characterization cell.

dual electrochromic systems could not exceed the contrast obtained from a single system, suggesting the use of an electroactive, yet nonelectrochromic, highly transmissive polymer as a counter electrode material.[35] Anodically coloring ProDOP derivatives are strong candidates for use as counter electrode materials because of their particularly pale color tones in all redox states, and in some cases as is exploited in the work reported here, owing to their electrochromic inactivity. We have previously shown that the band gaps for N-substituted PProDOPs are > 3.0 eV, forcing the $\pi-\pi^*$ transitions into the UV because of torsions induced along the heterocyclic backbone, making them highly transmissive over the entire visible spectrum.[36−39] Specifically, as shown in this manuscript, the *N*-propionitrile derivative (PProDOP-*N*-EtCN) exhibits strong electroactivity without changing color.

We have applied the dual-polymer electrochromic film characterization method in this work to establish a new color profile including black to transmissive by mixing a green and a purple polymer that can both switch to transmissive. We introduce the first black to transmissive switching conjugated polymer-based ECD, namely the pseudo 3-electrode electrochromic device (P3-ECD). This device adds colors by transmitting light through two working electrodes (coated with two different electrochromic polymer films) and two counter electrodes (coated with nonelectrochromic, yet electroactive, polymer films). The electrodes are placed under separate potentiostatic control enabling multicolor switching, and a full color palette to be obtained. In this work, we incorporate the non color-changing, highly transmissive, electroactive polymer PProDOP-*N*-EtCN as a counter electrode material. The P3-ECD stands out with its optical contrast comparable to both single polymer films used in individual EC cells. By utilizing the P3-ECD, one can envision not only black-to-white changing images but also colored images that can be displayed as information. The P3-ECD could also serve as a reflective type of device (i.e., e-book) or an electrochromic mirror using a diffuse or a specular back-plane, respectively.

Results and Discussion

In this work, PProDOT-ester and PProDOT-BTD were chosen as pure purple and green colored polymers, where their absorption spectra can be summed to provide new colors, including black. The repeat unit structures of the polymers, along with photographs of the polymer films in their oxidized and reduced states, and the schematic of the dual-polymer electrochromic method are shown in Figure 1.

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Electrochemical Characterizations. Understanding the electrochemical response and coloration process of each component polymer film is paramount in color and device engineering. Electrochemical characterizations on Pt-button electrodes, along with spectroelectrochemical and colorimetric experiments on ITO-coated glass electrodes, were used to define the optimum redox switching conditions. In order to obtain thin films of the EC polymers for electrochemical and optical studies, PProDOT-ester and PProDOT-BTD were drop-cast (on Pt-button electrodes) or spray-cast (on ITO-coated glass electrodes) from a 2 mg/mL polymer/toluene solution after being filtered through 0.45 μm PTFE filters. The films on ITO/glass were dried under vacuum overnight. PProDOP-*N*-EtCN was electrodeposited by potential scanning (20 cycles, 50 mV/s, −0.25 V to +0.60 V vs Fc/Fc$^+$, for Pt-button electrode (see Figure S1 in the Supporting Information) and 10 cycles, 50 mV/s, −0.3 V to +0.80 V vs Fc/Fc$^+$, for ITO-coated glass electrode). During the first anodic scan, a single irreversible monomer oxidation peak was observed at +0.4 V vs Fc/Fc$^+$ with redox responses evolving with multiple scans due to the polymer doping and dedoping process. PProDOP-*N*-EtCN films did not adhere strongly to ITO/glass, probably because of the *N*-substitution, which enhances solubility. To stabilize the polymer on the transparent electrode, we heated films at 55 °C under a vacuum for 30 min. All polymer films were conditioned under repeated potential scanning before use. Cyclic voltammograms (CV's) were recorded for each polymer at scan rates ranging from 25 to 300 mV/s, as shown in Figures S2−S4 (Supporting Information), to determine proper switching potentials. A linear increase of the current with scan rate is observed for each film, indicative of a surface adhered electroactive polymer film.

Spectroelectrochemistry. Spectroelectrochemistry was used to assess the electronic structure and the nature of electrochromism in the electrochromic polymers because polarons, bipolarons, and π-dimers all factor into their respective optical changes. Colorimetric studies were conducted to acquire the optical characteristics of the polymer films in the correct potential ranges determined by the CV experiments. The spectroelectrochemical series for each of the polymer films are shown in Figure 2. In their neutral states, PProDOT-ester appears purple (absorbing mainly at 574 nm), PProDOT-BTD appears green (absorbing at 465 nm and 707 nm), and PProDOP-*N*-EtCN appears transmissive (transmitting along the full visible region). As these polymer films are doped, charge carrier states emerge with the majority of the light absorption for each polymer being in the NIR, which results in highly transmissive films. In the case of PProDOT-BTD, plotted in Figure 2b inset, raising the potential from −0.35 to 0.55 V (vs Fc/Fc$^+$), the %*T* values for the short wavelength band (at 465 nm) increases from 12% to 64%, resulting in a 52% change in %*T*. This change in %*T* is limited to 36% at the long wavelength band (at 707 nm), starting from 4% in the neutral state and increasing to 40% as it is doped. This remnant absorption at the longer wavelength band results in a light blue hue in the transmissive state of the film. Considering both the green and the purple polymers, while the visible bands bleach during oxidative doping, the low energy carrier band tails back into the visible region and, thus, the truly bleached state is not observed. On the other hand, PProDOP-*N*-EtCN is transmissive over the entire visible region independent of redox state, while being highly electrochemically active as illustrated by the results in the inset to Figure 2c. The interesting behavior of PProDOP-*N*-EtCN is attributed to the conformational changes that lead to changes in the conjugation length. Although bulky substituents disrupt planarity and lower

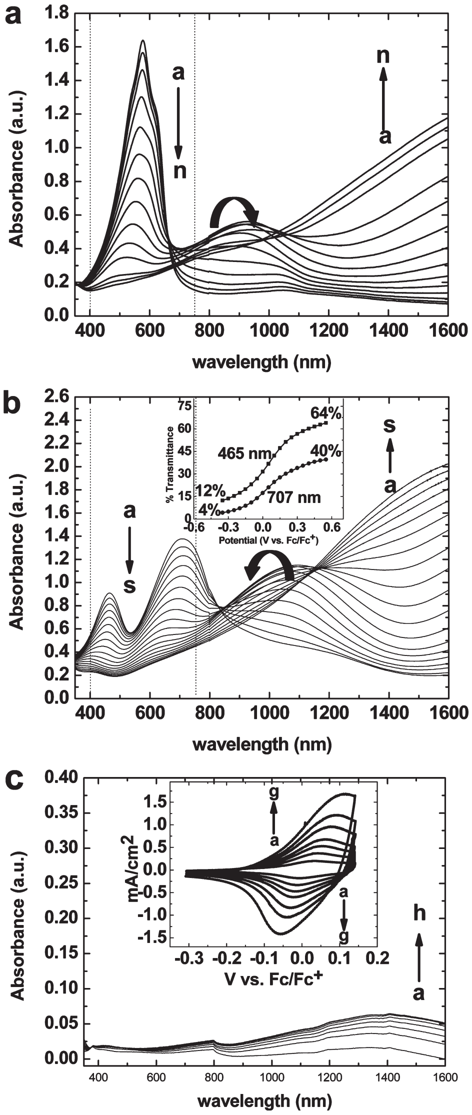

Figure 2. Spectroelectrochemistry of (a) spray-cast, redox switched, PProDOT-ester film at applied potentials of (a) −0.35 (b) −0.30 (c) −0.25 (d) −0.20 (e) −0.15 (f) −0.10 (g) −0.05 (h) 0.00 (i) +0.05 (j) +0.10 (k) +0.15 (l) +0.25 (m) +0.30, and (n) +0.35 V vs Fc/Fc$^+$;(b) spray-cast, redox switched, PProDOT-BTD film at applied potentials of (a) −0.35 to (s) +0.55 V vs Fc/Fc$^+$ at intervals of 50 mV; inset, change in %*T* as a function of applied potential for the two absorption bands (at 465 and 707 nm); and (c) potential-scan deposited, redox switched, PProDOP-*N*-EtCN film at applied potentials of (a) −0.08 to (h) +0.27 V vs Fc/Fc$^+$ at intervals of 50 mV; inset, cyclic voltammograms of PProDOP-N-EtCN in 0.1 M TBAP/PC at scan rates of (a) 25, (b) 50, (c) 75, (d) 100, (e) 150, (f) 200, and (g) 300 mV/s on a Pt-button.

Table 1. Coloration Efficiencies and Switch Times of PProDOT-ester and PProDOT-BTD at Various Film Thicknesses in 0.1 M TBAP/PC; Values are Reported at 95% of Full Switch

PProDOT-BTD						PProDOT-ester			
absorbance (au)	thickness (nm)	*CE* (cm^2/C)	$t_{0.95}{}^{a}$ (s)	*CE* (cm^2/C)	$t_{0.95}{}^{b}$ (s)	absorbance (au)	thickness (nm)	*CE*(cm^2/C)	$t_{0.95}{}^{c}$ (s)
0.42	180	333	1.2	485	0.4	0.19	190	651	1.0
0.59	220	291	2.3	317	1.3	0.64	360	758	2.0
0.84	290	284	1.5	414	1.2	0.93	470	692	1.4
1.17	380	299	1.0	430	1.2	1.03	500	707	2.2
1.68	520	237	2.1	568	1.8	1.40	640	855	1.6
1.82	560	296	2.1	428	2.3	1.79	790	780	2.9

$^{a-c}t_{0.95}$; switch times for 95% of full switch, CE; composite coloration efficiency, (*a*) at $\lambda = 465$ nm, (*b*) at $\lambda = 707$ nm, (*c*) at $\lambda = 574$ nm.

conjugation length, small *N*-substituents have much lower barrier to rotation. The onset of the $\pi-\pi^*$ transition is located at the boundary of the visible and ultraviolet regions of the spectrum, making the polymer colorless in its neutral state. Full oxidation to the bipolaronic states leads to charge repulsions and, as the *N*-substituent is relatively small, the doped polymer can attain a near-planar state. This red-shifts the bipolaron absorption well into the NIR.

Composite Coloration Efficiency. The composite coloration efficiency (*CCE*)[13] method was used to determine the preparation conditions for polymer films yielding the highest contrast ratios, and exhibiting similar switching times for application in the dual-film technique and P3-ECD. A tandem chronoabsorptometry/chronocoulometry experiment was used to calculate both the *CCE* and the switch times at 95% of the total optical change ($\Delta\%T$) at $\lambda_{\max}$. The composite coloration efficiencies were calculated from eq 1[12,13,40]

$$\eta = \frac{\Delta OD(\lambda_{\max})}{q_{\mathrm{d}}} \qquad (1)$$

In eq 1, ΔOD is the change in optical density and q_{d} is the injected charge per unit of electrode area as the polymer film completes 95% of its full switch. An ideal electrochromic material or device exhibits a large transmittance change with a small amount of charge.

The tandem chronocoulometry and chronoabsorptometry results for each of the films are shown in Figure 3 with the effect of film thickness on coloration efficiency and switching time illustrated in Table 1. Because the PProDOT-BTD's electrochromism is not limited to a single wavelength, the coloration efficiency was calculated at both $\lambda_{\max}$ values and, as such, the CE values of PProDOT-ester are higher than that observed for PProDOT-BTD. The PProDOT-ester film with a thickness of *ca.* 500 nm exhibited a switching charge density of 1.1 mC/cm^2 with a change in $\%T$ of 54% resulting in a *CE* of 707 cm^2/C at $\lambda_{\max}$ of 574 nm (Figure 3a), whereas the thinner PProDOT-BTD film (ca. 380 nm) has a charge density of 1.7 mC/cm^2 with a change in $\%T$ of 50% resulting in a *CE* of 299 cm^2/C at $\lambda_{\max}$ of 465 nm (Figure 3b) and a charge density of 1.6 mC/cm^2 with a change in $\%T$ of 40% resulting in a *CE* of 430 cm^2/C at $\lambda_{\max}$ of 707 nm (Figure 3c). Because the PProDOP-*N*-EtCN derivative is noncolor changing with a weak unsaturated color, the optical properties of the dual film systems and devices are dominated by the saturated colors of the cathodically coloring polymers.

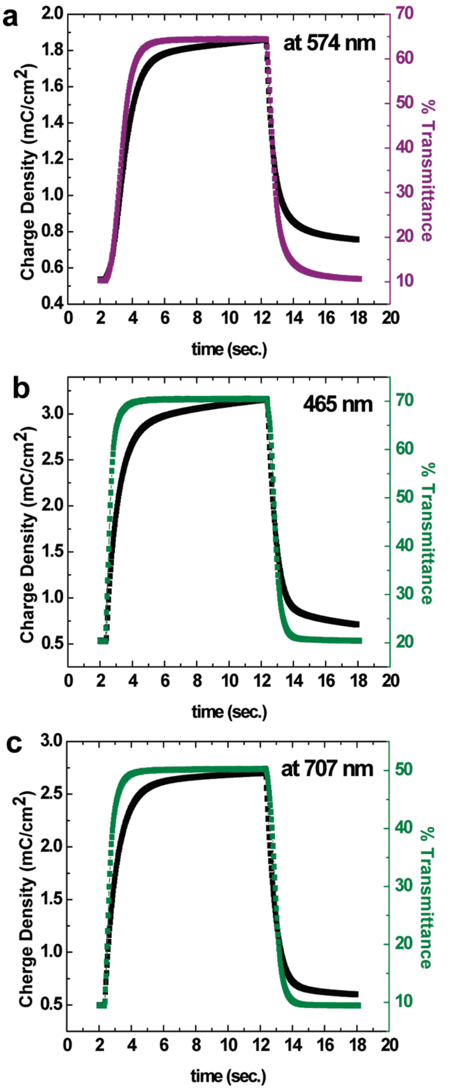

Figure 3. Tandem chronoabsorptometry and chronocoulometry experiments for (a) PProDOT-ester (stepped from −0.2 V to +0.4 V vs Fc/Fc$^+$, held for 10 s at each potential at 574 nm), (b) PProDOT-BTD (stepped from −0.30 to +0.60 V vs Fc/Fc$^+$, held for 10 s at each potential at 465 nm), and (c) PProDOT-BTD (stepped from −0.30 to +0.60 V vs Fc/Fc$^+$, held for 10 s at each potential at 707 nm) in 0.1 M TBAP/PC solution.

Switching times are dominated by the diffusion of the counterions through the films during redox. Fast optical

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[40] Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559.

response times (in seconds) were observed in these systems because the open morphology of the polymer (bulky structures) promotes the mobility of charge compensating counterions. The coloration efficiency is shown to be relatively independent of film thickness for these systems. This behavior is attributed to the balance of the increase in change of optical density, ΔOD, by the increase in charge density in these nicely performing EC polymers.

Colorimetry. In situ Colorimetry has been utilized to precisely map the colors associated with the EC polymers under investigation and was carried out with a portable colorimeter to yield color coordinates as CIE Yxy color space values, which were converted to $L^*a^*b^*$ color coordinates. High-contrast displays, as estimated by the ratio of the darkest color to the brightest color, are desired because they are much better perceived by the human eye. The contrast can arise either from luminance or color differences, and it is dependent on the illuminant and the viewing angle. The luminance contrast (Michelson contrast) can be calculated using eq 2

$$C = \frac{(Y_{\max} - Y_{\min})}{(Y_{\max} + Y_{\min})} \qquad (2)$$

where $Y_{\max}$ and $Y_{\min}$ are the luminance values for the brightest and darkest states, respectively.[42-44]

It is worth noting that using colors other than black and white in a display results in a reduced luminance contrast (see eq 2). The total color of a specified state, Q, can be calculated by eq 3, and the color contrast between two samples or states illuminated and viewed under the same conditions can be calculated from eq 4

$$Q = \sqrt{(L^{*2}) + (a^{*2}) + (b^{*2})} \qquad (3)$$

$$\Delta E_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (4)$$

where ΔL^*, Δa^*, and Δb^* represent changes in L^*, a^*, b^* (in this paper, they represent the differences between the colored and the bleached states of the films).[41]

The effect of thickness on color and contrast was studied by monitoring the relative luminance (% Y) values as a function of applied potential using films of various thicknesses (see optical absorbance/thickness calibration plots in the Supporting Information, Figure S5). Figure 4 demonstrates that the Michelson luminance contrast (C) increases with film thickness and those results were used to calculate the color contrast (ΔE). For PProDOT-ester, as the thickness increases from 190 to 790 nm, the luminance contrast increases from 0.2 to 0.8 and the color contrast increases from 17 to 78. For PProDOT-BTD, as the thickness increases from 150 to 520 nm, the luminance contrast increases from 0.1 to 0.5 and the color contrast increases from 14 to 38. Both the luminance and color contrast values were observed to increase as the film thickness increases to subsequently reach an optimum value. Upon doping, the bipolaron carrier bands shift into the NIR region by repressing the absorbance in the visible, thus the optical contrast increases. Thick films of sterically bulky structures can incorporate a high quantity of counterions to compensate for the oxidation, and therefore, as the thickness increases, the oxidized polymer maintains high luminance values, whereas the luminance in the reduced state decreases.

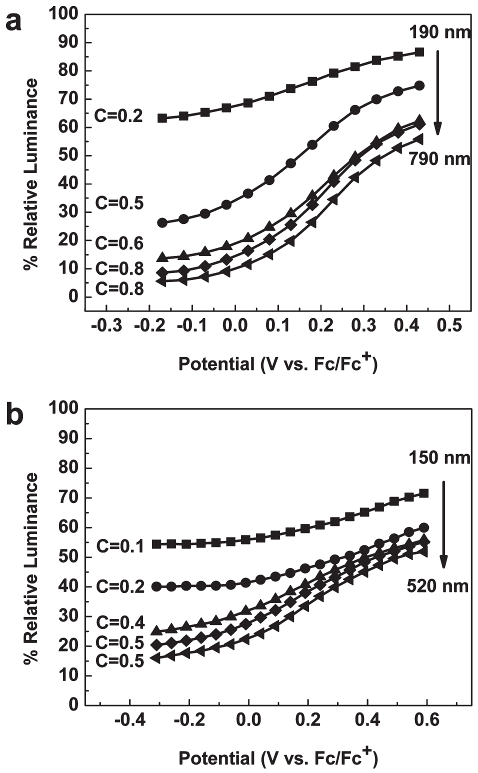

Figure 4. Percent relative luminance as a function of applied potential of (a) PProDOT-ester film at thicknesses of -■- 190 nm (0.2 au), -●- 360 nm (0.6 au), -▲- 500 nm (1.0 au), -◆- 640 nm (1.4 au), -▼- 790 nm (1.8 au); and (b) PProDOT-BTD film at thicknesses of -■- 150 nm (0.3 au), -●- 220 nm (0.6 au), -▲- 320 nm (1.0 au), -◆- 450 nm (1.4 au), -▼- 520 nm (1.7 au).

One of the major parameters to take into account in ECDs is their long-term optical stability in ambient conditions. Therefore, the stability of the optical changes occurring during switching of the EC polymers was investigated prior to dual-film studies and device construction. The stability experiments were performed by stepping the potential between the extreme redox states of the PProDOT-ester and PProDOT-BTD films (sprayed on ITO/glass) in 0.1 M TBAP/PC while monitoring their lightness (L^*) in both their fully oxidized and neutral states. The charge densities, q_{red}, associated with the neutralization of the films were simultaneously monitored. PProDOT-ester retained 50% of its optical response after 5000 double potential steps, whereas PProDOT-BTD retained 70% of its optical response after

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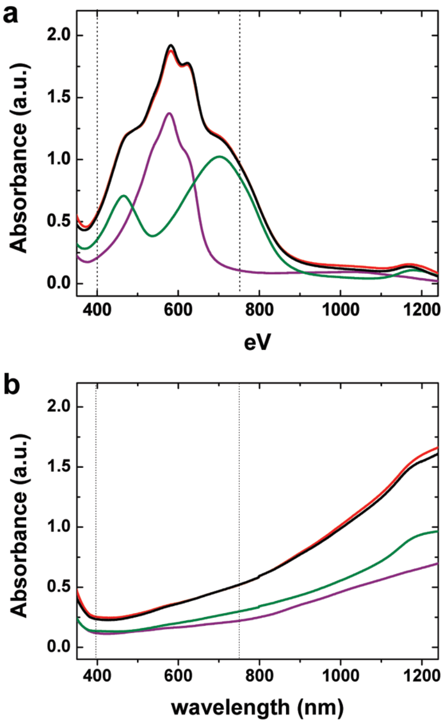


Figure 5. UV−vis−NIR spectra from PProDOT-ester/PProDOT-BTD dual-EC Method in 0.1 M TBAP/PC solution. (a) PProDOT-ester film-reduced (purple line) and PProDOT-BTD film-reduced (green line) and the theoretical sum of PProDOT-ester film-reduced and PProDOT-BTD film-reduced (red line) and the experimental sum of PProDOT-ester film-reduced and PProDOT-BTD film-reduced (black line); (b) PProDOT-ester film-oxidized (purple line) and PProDOT-BTD film-oxidized (green line) and the theoretical sum of PProDOT-ester film-oxidized and PProDOT-BTD film-oxidized (red line) and the experimental sum of PProDOT-ester film-oxidized and PProDOT-BTD film-oxidized (black line).

15 000 double potential steps, which are useful switching stabilities in air (see Figure S6 in the Supporting Information).

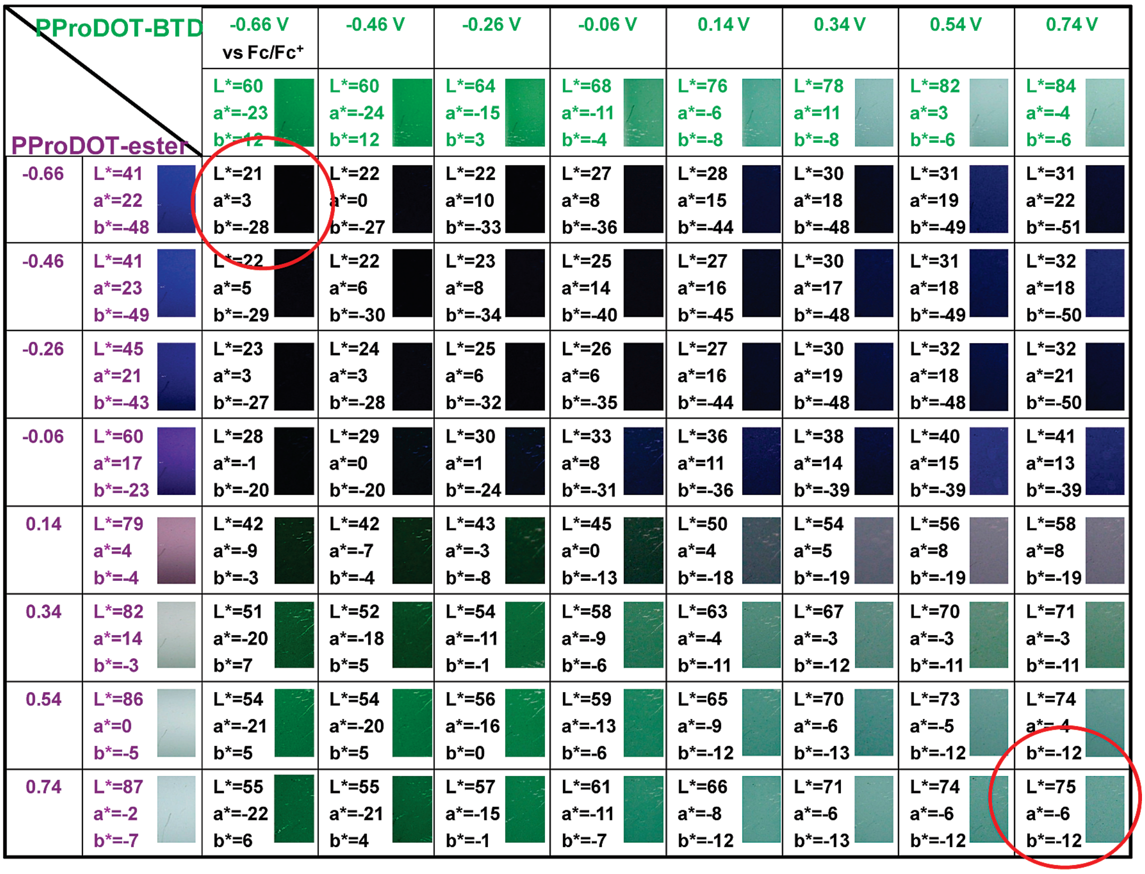
PProDOT-ester/PProDOT-BTD Dual EC-Film Characterization Method. The dual EC-film characterization method was utilized to predict the colors that could be generated by multielectrode devices whose working principles are based on color mixing. Both, PProDOT-ester and PProDOT-BTD on ITO electrodes under separate potentiostatic control were placed back to back in a 1 cm quartz cell and used as two working electrodes, with a Ag wire as the reference electrode and a Pt wire as the counter electrode. In situ color coordinates and spectra in the visible region were recorded from the dual-polymer system as the potential of each working electrode was varied independently in 0.1 M TBAP/PC.[33]

To gain insight into the addition of the optical properties by means of the dual-film EC method, we took absorbance spectra of both PProDOT-ester and PProDOT-BTD separately at fully reduced (both at −0.66 V vs Fc/Fc$^+$) and fully oxidized (both at +0.74 V vs Fc/Fc$^+$) states, and these spectra were summed theoretically. This is demonstrated by the single film purple and green curves in Figure 5, along with the theoretical summation represented by the red curve. The black curve shows the spectral response of the films combined in the dual-EC method. The theoretical and experimental spectra are shown to overlay one another for the oxidized and reduced films.

The dual-film system was subsequently studied colorimetrically in order to develop a full color palette. Photographs and $L^*a^*b^*$ color coordinates as a function of the separate potential applied to each film are shown in Figure 6 (note that appearance of PProDOT-ester is bluer than observed because of lab lighting conditions. Figure 1b shows a photograph with the proper purple tone). The film thicknesses were set to yield the optimum contrast by utilizing the contrast data reported earlier. As it was shown in Figure 4, the maximum contrast that could be obtained from PProDOT-ester is 0.8, whereas this value is only 0.5 for PProDOT-BTD. Therefore, PProDOT-ester with a thickness of 600 nm ($A = 1.3$ au) switching from deep purple ($L^* = 41$, $a^* = 22$, $b^* = -48$, $Q = 67$) to highly transmissive sky blue ($L^* = 87$, $a^* = -2$, $b^* = -7$, $Q = 87$) upon doping with $C = 0.7$ and $\Delta E = 66$ and PProDOT-BTD with a thickness of 360 nm ($A = 1.1$ au) switching from deep green ($L^* = 60$, $a^* = -23$, $b^* = 12$, $Q = 65$) to highly transmissive sky blue ($L^* = 84$, $a^* = -4$, $b^* = -6$, $Q = 84$) upon doping with $C = 0.4$ and $\Delta E = 36$ were utilized in multielectrode systems (see Figure 6).

The new color palette we established extends from deep blue-black ($L^* = 21$, $a^* = 3$, $b^* = -28$, $Q = 35$) to clear ($L^* = 75$, $a^* = -6$, $b^* = -12$, $Q = 76$) and embodies all tones of mixtures of green and purple. The luminance contrast for this color gamut is 0.9 and the color contrast is 69. Using this method, we demonstrate that color mixing improves both the luminance C, and color contrast ΔE. Furthermore, having two colors mixed, and having the absorbance extend across the full visible range (formation of black), eliminated to a noticeable extent any hindrance to contrast due to the chroma.

PProDOT-ester/PProDOT-BTD/PProDOP-*N*-EtCN P3-ECD. Using this broadly absorbing set of complementary polymers, we have applied the dual-EC method to electrochromic devices. The P3-ECD that we propose can be utilized either as a window type device or as a display by incorporating a reflective background. Physically, the construction of the P3-ECD is similar to dual absorptive/transmissive windows in that it consists of two absorptive/transmissive windows in series whose counter electrodes are shorted. (Figure 7) PProDOT-ester, PProDOT-BTD and PProDOP-*N*-EtCN films on ITO electrodes were prepared as described before. The thicknesses of PProDOP-*N*-EtCN films on the counter electrodes were set to ensure charge balance with the polymer it was facing, along with retaining high transmissivity. All polymer films were electrochemically conditioned by sweeping the potential between their extreme redox states. Cathodically coloring PProDOT-ester and PProDOT-BTD were fully oxidized (brought to their transparent state), whereas the non-color-changing films of PProDOP-*N*-EtCN were fully neutralized to set the charge balance prior to device assembly. The PProDOT-ester and PProDOT-BTD films were then coated with gel



PProDOT-BTD / PProDOT-ester		-0.66 V vs Fc/Fc$^+$	-0.46 V	-0.26 V	-0.06 V	0.14 V	0.34 V	0.54 V	0.74 V
		L*=60 a*=-23 b*=12	L*=60 a*=-24 b*=12	L*=64 a*=-15 b*=3	L*=68 a*=-11 b*=-4	L*=76 a*=-6 b*=-8	L*=78 a*=11 b*=-8	L*=82 a*=3 b*=-6	L*=84 a*=-4 b*=-6
-0.66	L*=41 a*=22 b*=-48	L*=21 a*=3 b*=-28	L*=22 a*=0 b*=-27	L*=22 a*=10 b*=-33	L*=27 a*=8 b*=-36	L*=28 a*=15 b*=-44	L*=30 a*=18 b*=-48	L*=31 a*=19 b*=-49	L*=31 a*=22 b*=-51
-0.46	L*=41 a*=23 b*=-49	L*=22 a*=5 b*=-29	L*=22 a*=6 b*=-30	L*=23 a*=8 b*=-34	L*=25 a*=14 b*=-40	L*=27 a*=16 b*=-45	L*=30 a*=17 b*=-48	L*=31 a*=18 b*=-49	L*=32 a*=18 b*=-50
-0.26	L*=45 a*=21 b*=-43	L*=23 a*=3 b*=-27	L*=24 a*=3 b*=-28	L*=25 a*=6 b*=-32	L*=26 a*=6 b*=-35	L*=27 a*=16 b*=-44	L*=30 a*=19 b*=-48	L*=32 a*=18 b*=-48	L*=32 a*=21 b*=-50
-0.06	L*=60 a*=17 b*=-23	L*=28 a*=-1 b*=-20	L*=29 a*=0 b*=-20	L*=30 a*=1 b*=-24	L*=33 a*=8 b*=-31	L*=36 a*=11 b*=-36	L*=38 a*=14 b*=-39	L*=40 a*=15 b*=-39	L*=41 a*=13 b*=-39
0.14	L*=79 a*=4 b*=-4	L*=42 a*=-9 b*=-3	L*=42 a*=-7 b*=-4	L*=43 a*=-3 b*=-8	L*=45 a*=0 b*=-13	L*=50 a*=4 b*=-18	L*=54 a*=5 b*=-19	L*=56 a*=8 b*=-19	L*=58 a*=8 b*=-19
0.34	L*=82 a*=14 b*=-3	L*=51 a*=-20 b*=7	L*=52 a*=-18 b*=5	L*=54 a*=-11 b*=-1	L*=58 a*=-9 b*=-6	L*=63 a*=-4 b*=-11	L*=67 a*=-3 b*=-12	L*=70 a*=-3 b*=-11	L*=71 a*=-3 b*=-11
0.54	L*=86 a*=0 b*=-5	L*=54 a*=-21 b*=5	L*=54 a*=-20 b*=5	L*=56 a*=-16 b*=0	L*=59 a*=-13 b*=-6	L*=65 a*=-9 b*=-12	L*=70 a*=-6 b*=-13	L*=73 a*=-5 b*=-12	L*=74 a*=-4 b*=-12
0.74	L*=87 a*=-2 b*=-7	L*=55 a*=-22 b*=6	L*=55 a*=-21 b*=4	L*=57 a*=-15 b*=-1	L*=61 a*=-11 b*=-7	L*=66 a*=-8 b*=-12	L*=71 a*=-6 b*=-13	L*=74 a*=-6 b*=-12	L*=75 a*=-6 b*=-12

Figure 6. *L*a*b** color coordinates and photography for PProDOT-ester/PProDOT-BTD in 0.1 M TBAP/PC (all potentials are reported vs Fc/Fc+).

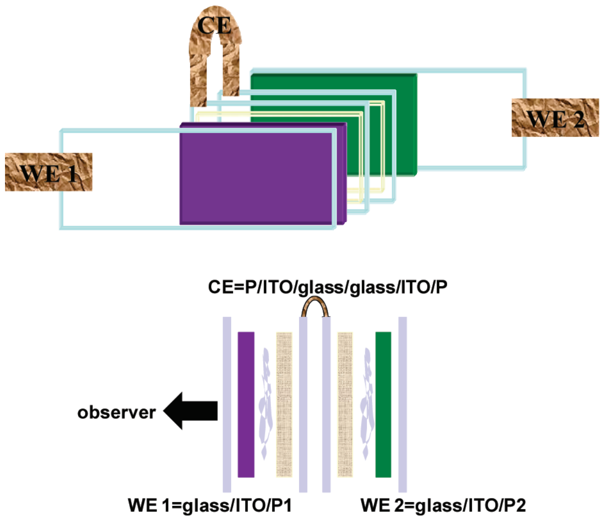


Figure 7. Schematic of P3-ECD under bipotentiostatic control.

electrolyte, and the PProDOP-*N*-EtCN films were layered on top of them. The PProDOT-ester then serves as working electrode-1 and PProDOT-BTD serves as working electrode 2. The devices were encapsulated by paraffin wax and epoxy to allow long-term testing. In situ color coordinates were then recorded from the P3-ECD upon application of varied potentials to the two different working electrodes.

The absorbance spectra and the colorimetric data with photographs obtained from the P3-ECD is shown in Figures 8 and 9. Examining the spectra, the PProDOT-ester/PProDOT-BTD device shows a broad absorption with multiple peaks over the entire visible range upon reduction of both EC working electrode polymers. When a potential of 1.4 V is applied to both WE1 (PProDOT-ester) and WE2 (PProDOT-BTD) films, the device becomes highly transmissive ($L^* = 75, a^* = -7, b^* = -7$) and when a potential of -0.2 V is applied to both working electrodes, both films become absorptive and the device appears blue-black absorbing along the full visible region ($L^* = 26, a^* = -3, b^* = -17$). When a potential of -0.2 V is applied to WE1 (PProDOT-ester) and 1.4 V to WE2

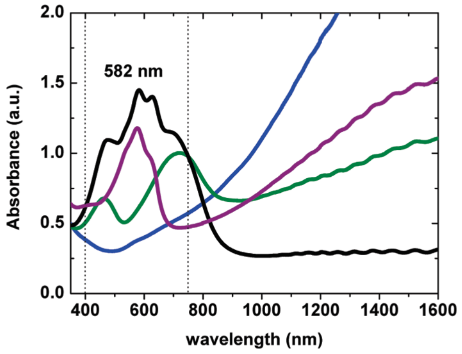
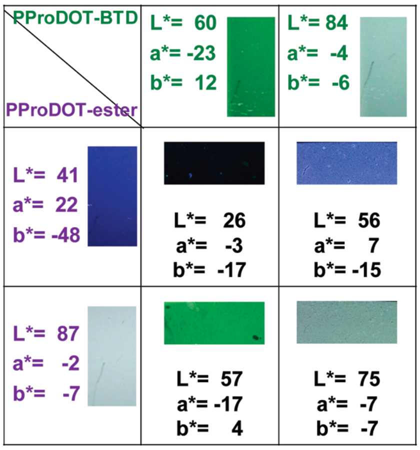


Figure 8. UV−vis−NIR spectra of the P3-ECD. Working electrode 1 (coated with PProDOT-ester) reduced (purple line), working electrode 2 (coated with PProDOT-BTD) reduced (green line), both of the working electrodes reduced (black line), and both working electrodes oxidized (blue line).



PProDOT-BTD PProDOT-ester	L*= 60 a*= -23 b*= 12	L*= 84 a*= -4 b*= -6
L*= 41 a*= 22 b*= -48	L*= 26 a*= -3 b*= -17	L*= 56 a*= 7 b*= -15
L*= 87 a*= -2 b*= -7	L*= 57 a*= -17 b*= 4	L*= 75 a*= -7 b*= -7

Figure 9. $L^*a^*b^*$ color coordinates and photography for PProDOT-ester/PProDOT-BTD P3-ECD.

(PProDOT-BTD), the green film becomes transmissive and the device appears deep purple ($L^* = 56$, $a^* = 7$, $b^* = -15$). When a potential of −0.2 V is applied to WE2 (PProDOT-BTD) and 1.4 V to WE1 (PProDOT-ester), the green film becomes absorptive, and the purple film becomes transmissive, allowing the device to appear deep green ($L^* = 57$, $a^* = -17$, $b^* = 4$). The P3-ECD device shows a luminance contrast of 0.8 and a color contrast of 50.

With L^* values changing from 26 to 75 upon bleaching, the P3-ECD exhibits a reasonable contrast value and suggests this device architecture may prove useful for simple display technologies, while also offering access to additional colors. In a preliminary study, we have shown that the device shows a reasonable stability to redox cycling. Here, the device was potential stepped between its darkest and brightest states and retained 50% of its optical contrast after 1000 deep potential cycles. This experiment was carried out on a device constructed and tested under an ambient atmosphere. As the counter electrode material, PProDOP-N-EtCN, has a low oxidation onset of −0.15 V vs Fc/Fc$^+$ it is prone to oxidation. Device encapsulation will be expected to enhance the stability significantly.

Conclusions

This work applies the “dual-polymer electrochromic film characterization under bipotentiostatic control method” that was demonstrated in an earlier paper[33] to a new type of device, namely the P3-ECD. This original pseudo 3-electrode device enables access to a broad palette of colors, as well as to a transmissive state by independently applying a potential to multiple active films. The dual polymer film technique and P3-ECD reported herein possess the ability to combine colors, and operate at low potentials. At their neutral states, PProDOT-BTD absorbs in the red and blue regions, and PProDOT-ester absorbs in the green region, and they become transmissive as they are oxidized. The two polymers were coupled by means of P3-ECD to result in a display that could absorb over the entire visible spectrum in the neutral state of the cathodically coloring polymer and switches to transmissive as the polymer is oxidized. Thus, the P3-ECD is the first device to demonstrate black-to-transmissive switching by color mixing with a luminance contrast as high as 0.8. In addition to dark-light contrast, the described P3-ECD offers a full palette of colors. Other than black and white, colored images could be displayed by P3-ECD.

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Supporting Information Available: Experimental details, electrochemical data, absorbance vs thickness linear fit plots, and polymer film optical stability plots (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.