4460 *Macromolecules* **2010**, *43*, 4460–4467
DOI: 10.1021/ma100366y

Macromolecules
ARTICLE

Orange and Red to Transmissive Electrochromic Polymers Based on Electron-Rich Dioxythiophenes

Aubrey L. Dyer,*,[†] Michael R. Craig,[†,‡] Joseph E. Babiarz,[‡] Kelly Kiyak,[‡] and John R. Reynolds*,[†]

[†]*The George and Josephine Butler Polymer Laboratories, Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville Florida, 32611, and* [‡]*BASF, Tarrytown, New York, 10591*

Received February 15, 2010; Revised Manuscript Received April 12, 2010

ABSTRACT: As the color palette of available solution processable electrochromic polymers expands, there has remained the need for red, orange, and yellow to transmissive switching materials. Here we report on the synthesis and characterization of two such polymers, the orange to transmissive switching (poly{3,4-di(2-ethylhexyloxy)thiophene}) electrochromic polymer-orange (ECP-orange) and the red to transmissive switching processable polymer (poly{3,4-di(2-ethylhexyloxy)thiophene-*co*-3,4-di(methoxy)thiophene}) electrochromic polymer-red (ECP-red). The ECP-orange has a bandgap of 2.04 eV, an absorption λ_{max} centered at 483 nm, and an $E_{1/2}$ of 0.37 V versus Ag/Ag^+. The electrochromic contrast is 48% T at 483 nm with a time to reach 95% of the full optical contrast of 5.3 s for a film that has an absorbance of 0.98 au at λ_{max}. Because of steric relaxations from the random copolymerization of a branched dialkoxy-substituted thiophene with a dimethoxy-substituted thiophene, the red to transmissive switching ECP-red has a bandgap of 2.00 eV, a λ_{max} red-shifted by 42 to 525 nm, and an $E_{1/2}$ decreased to 0.21 V versus Ag/Ag^+. Additionally, the red polymer has a higher contrast of 60% T and a shorter time to reach 95% of the full optical contrast of 2.3 s. These two reported polymers allow the field of electrochromics to come closer to a full set of fully solution processable materials that yield films whose optical absorption covers the full visible spectrum while switching to a highly transmissive oxidized state as needed for full color displays.

Introduction

Electrochromic materials have held the attention of the scientific community, namely, in the smart windows and dynamic displays areas, for several decades now.[1−7] The most commonly cited materials are those that include the metal oxides (e.g., tungsten trioxide, WO_3) and viologen compounds (e.g., 4,4′-dimethylviologen) but also include transition metal complexes and conjugated electroactive polymers.[1,2,8] Whereas many of the known electrochromic materials have received extensive research efforts and attempts toward commercialization (some quite successfully), there remain drawbacks. These include electrochromes that are solution-based, limiting application in devices, such as some viologens, and transition-metal complexes (e.g., $Ru(bpy)_3^{2+}$), whereas other materials have relatively slow switching speeds, as with the metal oxides that require anywhere from 30 s to several minutes to reach a full contrast,[9] limiting their application in devices that require a color change at shorter time frames. Other drawbacks include lack of ease of processability to high surface area or patterned films (as needed for windows and displays) and limit in range of colors available. Through intensive synthetic efforts over the past 5−10 years, conjugated electroactive polymers have come to address and remedy many of these drawbacks, with efforts still underway, to allow for fully solution processable, fast, and stable switching thin films that are available in colors that span the entire visible region, switching to highly transmissive states.[8,10]

There are a large number of examples of polymers with neutral state absorbances that vary across the visible region such as with the highly color-tunable azomethines of the Skene group,[11−13] and the multiply colored bis-heterocycle arylene polymers of this group.[14−17] Additionally, polymers have been reported with neutral state absorbances ranging from the UV for *N*-substituted poly(3,4-propylenedioxypyrroles)[18] to the near-infrared (NIR) for the low-gap polymers such as the donor−acceptor systems based on dithienopyrrole,[19,20] with colors in between that range from orange (e.g., bis(thienyl pyrrole)-9*H*-carbazole from Icli),[21] to red (e.g., poly(3-methylthiophene)), blue (e.g., poly(3,4-ethylenedioxythiophene) (PEDOT)),[22] and green (e.g., poly(2,7-carbazole) derivatives from the Leclerc group),[23] and poly(bis-EDOT-pyridines) of this group.[24]

However, for full color displays and window-type applications, it is required that the materials switch between colored and noncolored highly transmissive states, of which a limited sampling of electrochromic systems is available. Of the systems that are available, one of the most well-known and well-utilized colored to transmissive-switching electroactive polymers is PEDOT.[22,25] This polymer can be formed by electropolymerization from the monomer to deposit uniform films that switch from dark blue in the neutral state to highly transmissive, light blue in the oxidized state. Other colored to transmissive-switching polymers include the alkylenedioxypyrroles, such as poly(3,4-ethylenedioxypyrrole) (PEDOP), which is red in the neutral state and poly(3,4-propylenedioxypyrrole) (PProDOP), which is orange in the neutral state, with both switching to transmissive in the oxidized state.[18]

Whereas these materials switch effectively from vibrant colored states to highly transmissive oxidized states, a lack of solution processability limits their application in many respects as depositing homogeneous films across large area electrodes is

---

*Corresponding authors. Tel: (352)392-2012. Fax: (352)392-9741. E-mail: adyer@chem.ufl.edu, reynolds@chem.ufl.edu.

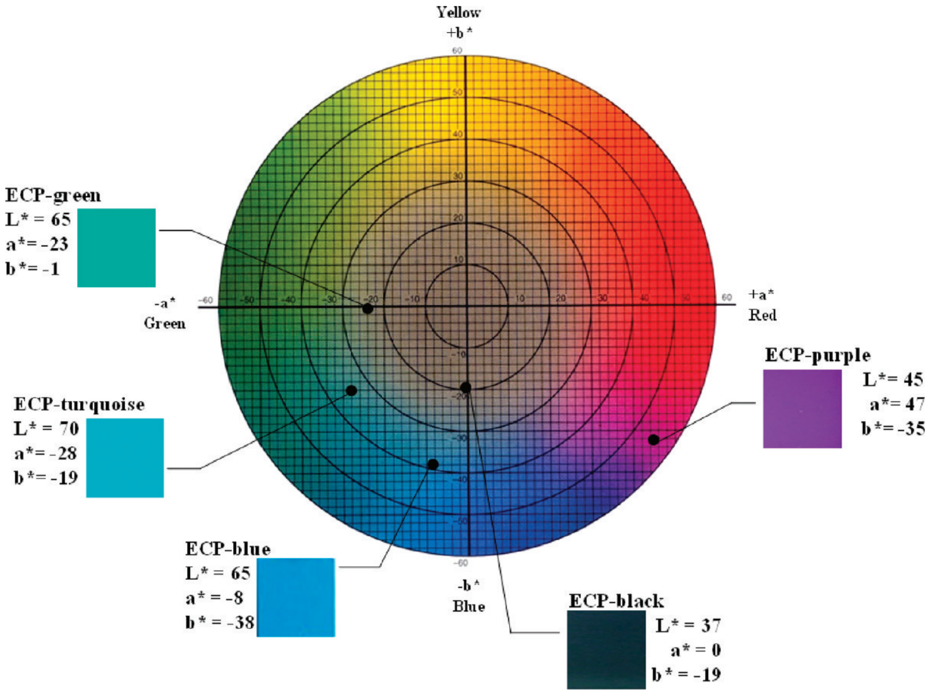


Figure 1. CIE 1976 LAB color plot with the a*b* values for recently published solution processable conjugated polymers reported by our group. The polymers represented here were chosen such that their oxidized, transmissive state have a*b* values less than ±5, indicating a near colorless oxidized state. L*a*b* values are reported in the literature for ECP-purple,[27] ECP-black,[35] ECP-blue,[34] ECP-turquoise,[31] and ECP-green.[31].

difficult and costly by electropolymerization. For ultimate ease of processing and device fabrication, soluble polymers that can be cast as uniform films are desired. Recent examples of solution processable colored to transmissive switching polymers include the alkyl- and alkoxy-substituted propylenedioxythiophenes (PProDOTs) from our group,[26,27] and the donor−acceptor systems such as the green to transmissive polymers from Toppare[28,29] and our group.[30,31]

In addition to the purple to transmissive switching PProDOT homopolymers and the green to transmissive ProDOT-benzothiadiazole-based donor−acceptor−donor polymers mentioned, our group has also focused attention on the synthesis of other fully solution processable multicolored electrochromic polymers (ECPs) that switch to highly transmissive, as illustrated by the a*b* color representation in Figure 1. This set of ECPs has been named as the family of SprayDOT ECPs.[32] Whereas we have been successful in obtaining colors that include purple,[26,27,33] blue,[34] turquoise,[30,31] green,[30,31] and even black,[35] it is noted that until now the top half of this color representation is empty.

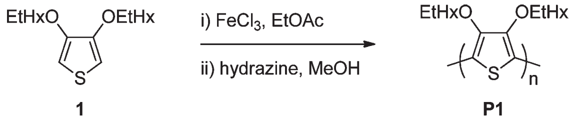
One reason for a lack of shorter wavelength absorbing materials (those which are red, orange, and yellow) that switch to transmissive is that while the absorbance shifts to longer wavelengths on oxidation of these polymers, it is still present in the visible region as with poly(3-methylthiophene), hence the large number of ECPs that have neutral state absorbances localized to wavelengths longer than 550 nm giving them a blue or purple color. To allow efficient depletion of the visible region absorbance on oxidation the electronic transitions must then occur largely in the NIR, as occurs with PEDOT and ECP-purple, for example. To allow completion of the full color palette of solution processable, colored to transmissive materials, judicious selection and tailoring of the polymer backbone is required such that the polymer exhibits higher energy absorbances at wavelengths shorter than 500 nm, but the charge carriers (polarons and bipolarons) become highly delocalized as the polymer conformation planarizes, shifting the absorbances out of the visible region.

Here we report the synthesis and electrochromic characterization of two such materials based on dialkoxy-substituted thiophenes that bring us closer to completing the color palette. A homopolymer of bis(ethylhexyloxy)thiophene (ECP-orange) that switches from a highly saturated orange to near colorless transmissive is demonstrated. The electron-donating effect of the disubstitution of two oxygens directly on the thiophene ring allows for lowering of the oxidation potential to near that of PEDOT, whereas branched alkyl groups induce solubility and steric distortion of the neutral polymer backbone, shortening the conjugation length and subsequently shifting the absorbance to ~480 nm. Additionally, a 1:1 copolymer of bis(ethylhexyloxy)thiophene and dimethoxythiophene (ECP-red) was prepared with a red neutral state that switches to a near colorless transmissive oxidized state at a low oxidation potential. Conversely, the random incorporation of branched alkyl and short methoxy substituents eases steric interactions, allowing for lengthening of the average conjugation length, which red shifts the neutral state absorbance by ~40 nm relative to ECP-orange. Electrochemical, spectroscopic, and full colorimetric characterizations are given for both of these polymers, allowing the field to come closer to full-color display applications.

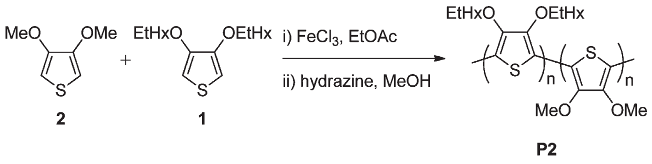
Results and Discussion

Synthesis. The polymers were prepared by oxidative coupling of the relevant dialkoxythiophene monomers with excess iron(III) chloride in ethyl acetate at room temperature, with subsequent reduction by hydrazine. The choice of ethyl acetate as solvent exploits the excellent solubility of iron(III) chloride in this medium, affording an initially homogeneous reaction mixture, which polymerizes rapidly. It is notable that the conventional solvent system of chloroform, or a mixture of chloroform and methanol, retards polymerization of these dialkoxythiophene moieties.[36−38] A five-fold excess of oxidant is employed to keep the oxidizing strength of the reaction sufficiently high to maximize yield and molecular weight.

Scheme 1. Synthesis of ECP-Orange (P1)



Scheme 2. Synthesis of ECP-Red (P2)



In the case of ECP-orange (**P1**), a very high molecular weight with low polydispersity is achieved (M_n ca. 115−153 kDa, PDI = 1.27 to 1.79) whereas ECP-red (**P2**) exhibits a lower molecular weight and broader polydispersity (M_n ca. 11−16 kDa, PDI = 2.12−4.38) (Schemes 1 and 2). The yield of ECP-red is consistently modest in the range of 20−30%, with losses incurred through removal of insoluble material of higher molecular weight by filtration. We suspect that the lower molecular weight of ECP-red relative to ECP-orange is due to the decreased conformational entropy of the di(methoxy)-thiophene monomer unit relative to the di(ethylhexyloxy)-thiophene unit resulting in a lower overall solubility of the copolymer in the reaction medium and thus limiting the propagation of the polymer chain and broadening the polydispersity. Whereas we expect the polymerization proceeds in a near random manner, comparison of the integrals in ^{1}H NMR confirms the 1:1 ratio of 3,4-dimethoxythiophene to 3,4-di(2-ethylhexyloxy)thiophene moieties in ECP-red, as shown in the Supporting Information. Both polymers have good solubility in solvents for film-casting (in particular spray casting) and demonstrate excellent film-forming characteristics.

Electrochemistry. The polymers were dissolved to a concentration of 1 mg/mL in either toluene for ECP-red or dichloromethane for ECP-orange. Thin films of each polymer were prepared on Pt button electrodes ($A = 0.02$ cm^2) by drop-casting from the polymer solution and allowing the solvent to slowly evaporate by placement of the inverted electrode in a draft-free environment. Once the solvent had fully evaporated, cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were performed in a 0.2 M lithium bis(trifluoromethyl)sulfonylimide (LiBTI)/propylene carbonate (PC) electrolyte with a Pt flag counter electrode and Ag/Ag$^+$ reference electrode, as described in the Experimental Methods section. The orange polymer required a break-in cycling of ~5−10 full cycles depending on the thickness of polymer deposited (Supporting Information), whereas the red polymer did not require break-in cycling. This result is not unexpected because of the high polymer molecular weight of ECP-orange contributing to a more densely packed film restricting full ion−solvent penetration on initial scans. On multiple scans, the morphology of the film opened up, and full electrochemical access is achieved repeatedly. Attempts to confirm this using microscopy methods were not fruitful because average feature sizes of the spray-cast films were not large enough to visualize using scanning electron microscopy (the films seem to be smooth). Preliminary atomic force microscopy studies[39] provide a topographic view of the films but do not elucidate changes occurring with switching break in.

The CV and DPV results for both polymers are shown in Figure 2A−D. ECP-orange exhibits an $E_{1/2}$ of 0.37 V versus Ag/Ag$^+$ and a peak-to-peak separation of 0.39 V, whereas ECP-red polymer has an $E_{1/2}$ of 0.21 V versus Ag/Ag$^+$ and a peak-to-peak separation of 0.04 V. The smaller peak-to-peak separation for ECP-red can be attributed to the faster electron exchange between redox sites within the polymer film and the working electrode surface. This is possibly due to either the easier movement of the electrolyte within the film of ECP-red or the smaller degree of structural rearrangement of ECP-red when cycled between neutral (nonplanar conformation) and oxidized (planar conformation) states.

The redox potentials for these polymers fall in the same potential range for similar thiophene-based polymers, such as 0.26 V versus Ag/Ag$^+$ for poly(3,4-dipropyloxythiophene) and 0.39 V versus Ag/Ag$^+$ for poly(3,4-dioctyloxythiophene).[40] The >150 mV higher redox potential for the orange polymer relative to red is attributed to the pendant group bulkiness and has been noted in similar disubstituted thiophene systems in the literature, where, for example, poly(3,4-dibutoxythiophene) has a 100 mV higher oxidation potential than poly(3-butoxy-4-methylthiophene).[41] Whereas the 3- and 4-substitutions of the electron-donating oxygen on the thiophene leads to a reduced oxidation potential in relation to an alkyl-substituted polymer, disubstitution with bulky branched alkoxy groups leads to increased steric interactions in the orange polymer resulting in a torqueing of the backbone, shortening the mean conjugation length and subsequently shifting the oxidation potential to a higher value. Random incorporation of 3,4-dimethoxythiophene with 3,4-bis-ethylhexyloxy thiophene in the red polymer relieves some of the steric strain, giving a longer mean conjugation in the polymer and a lower oxidation potential and is further seen in the optical results given later. As a preliminary test for electrochromic utility, both polymers were subjected to repeated electrochemical cycling (200 scans), as is shown in the Supporting Information, and exhibited little change in redox properties.

Spectroelectrochemistry. Films were spray-cast from solutions containing the polymer dissolved to a concentration of 5 mg/mL in dichloromethane for ECP-orange and toluene for ECP-red. Spray-casting was performed until the desired absorption maximum was achieved (between 0.6 and 1.4 au). The films appeared homogeneous and even to the eye, as evident by the homogeneity in the photos in Figure 3.

Spectroelectrochemistry was performed in situ by measuring the absorption spectrum of previously broken-in polymer films spray-cast onto ITO/glass slides with a Pt wire counter and Ag wire pseudo reference electrode (calibrated with the Fc/Fc$^+$ standard redox couple, which is found to be −0.29 to −0.30 V relative to Ag/Ag$^+$) in 0.2 M LiBTI/PC contained in a cuvette. During spectroelectrochemical measurement, the desired potential was applied to the film and held with the increments of each potential step being between 10 and 20 mV. As can be seen in Figure 4A, ECP-orange has a $\lambda_{\max}$ centered at 483 nm with an absorption onset at 607 nm corresponding to an optical bandgap of 2.04 eV. As each potential is stepped, the absorption in the NIR begins to increase, whereas that in the visible decreases, indicating the creation of lower energy polaron and bipolaron charge carriers at the expense of the π-to-π^* transition. When fully oxidized, the polymer has a strong absorption in the NIR that tails into the visible, giving the polymer a highly transmissive yet faint blue color due to residual red light absorbance. A noteworthy feature of this polymer is the large optical change in both the visible and NIR between a small potential step of 30 mV when stepped from 0.39 and 0.42 V, with a contrast of 76.9% at 1650 nm. We speculate that this large change in optical absorption over a small voltage range may be due to a cooperative intramolecular domino effect

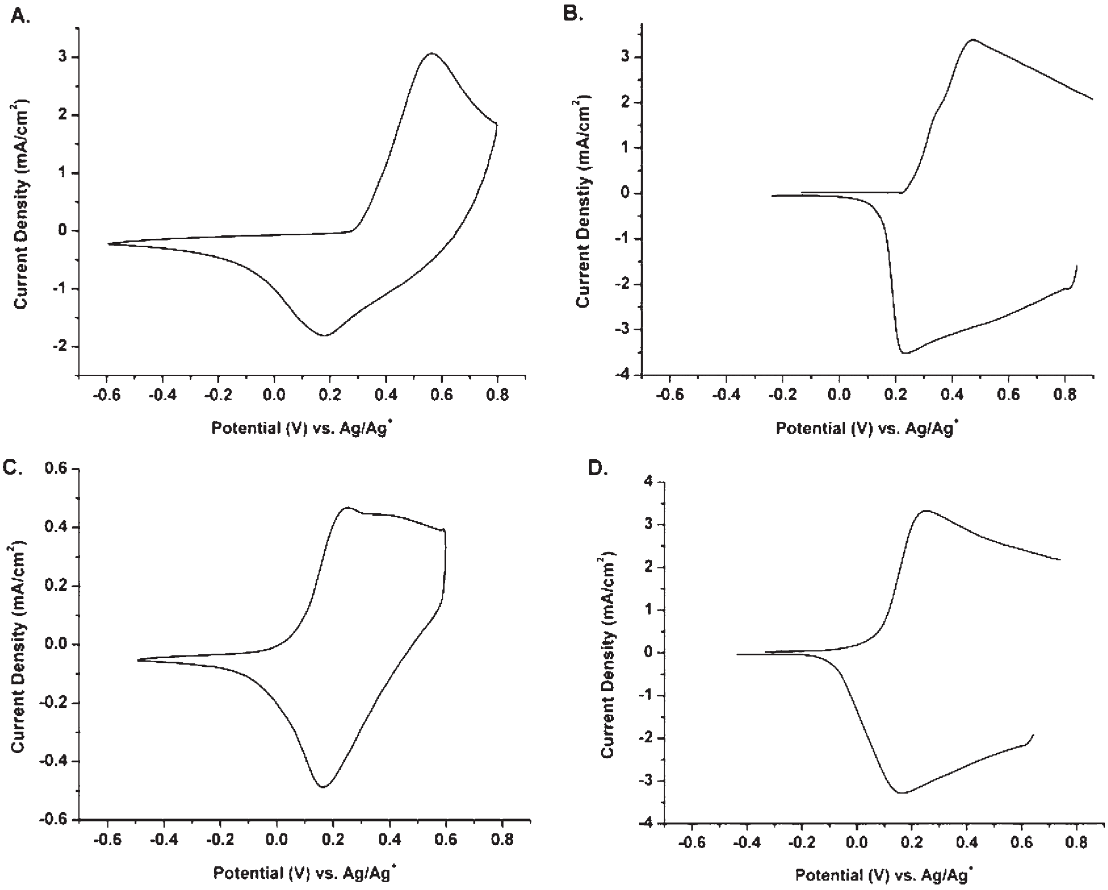


Figure 2. (A) CV and (B) DPV of a drop-cast film of ECP-orange from 1 mg/mL dichloromethane. (C) CV and (D) DPV of ECP-red drop-cast from 1 mg/mL in toluene. Electrochemistry was performed in a 0.2 M LiBTI/PC electrolyte at a 0.02 cm^2 Pt button electrode. Cyclic voltammetry carried out at a scan rate of 35 mV/s. The counter electrode was a Pt flag and the reference a Ag/Ag$^+$ (0.26 V versus SCE).

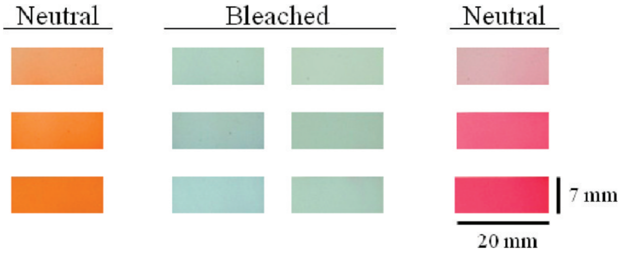


Figure 3. Photographs of films of ECP-red and ECP-orange in either a fully neutralized or fully oxidized state. The far left column is of ECP-orange of increasing optical density proceeding down the column (0.59, 0.98, and 1.2 au). The second column is of the same polymer films in the fully oxidized state. The third column is of the fully oxidized state of films of ECP-red (increasing optical density down the column, 0.30, 0.98, and 1.6 au) and the far right column is of the neutralized ECP-red films. The polymers were spray-cast onto ITO/glass (7 × 50 mm^2) and switched in 0.2 M LiBTI/PC while illuminated from behind with a D50 light source.

similar to the "twistons" described by Leclerc for the thermochromism of alkyl- and alkoxy-substituted thiophenes.[42,43] In the neutral state, the polymer exists in a nonplanar (less conjugated) form, and at initially low applied potentials, a low concentration of localized portions of the polymer chain become oxidized to a more planar (highly conjugated) form. However, as the applied potential is increased and a higher concentration of repeat units becomes oxidized, a cooperative mechanism comes into play where the twisting of these first repeat units to the more planar conformation induces a twisting of a larger number of neighboring units. This is in contrast with ECP-red, where the oxidation proceeds with a monotonic change in the optical transitions, as seen in Figure 4B for the spectroelectrochemical series of ECP-red. This polymer has a $\lambda_{\max}$ in the neutral state of 525 nm and an absorption onset of 620 nm corresponding to a bandgap of 2.0 eV with lower energy electronic transitions emerging on oxidation at the expense of the π-to-π^* transition.

Electrochromic Contrast and Switching Speed. The difference in the ease with which the two polymers are oxidized is also evident in Figure 5A,B, which shows the change in transmittance measured as the rate of switching the polymer film, between fully oxidized and neutralized, is increased. Specifically, for ECP-orange, as the polymer is switched between the potentials of −0.73 and 0.57 V with a 30 s hold at each potential, the percent transmittance (%*T*) contrast is 47.2%. As the time the oxidizing and reducing potentials are held is decreased to 10 s, the contrast decreases only slightly to 44.9% and subsequently to 42.6% for a 5 s hold, 13.6% for a 1 s hold, and 7.4% for a half second hold. As for ECP-red, when switched between −0.72 and 0.38 V versus Ag/Ag$^+$, the contrast is 60.6% for a 30 s hold, 60.2% for 10 s, 59.9% for 5 s, 30.6% for 1 s, and 16.5% for half second hold. A direct comparison of the switching speeds for these two films can be made as the optical density of each polymer at $\lambda_{\max}$ in the neutral state is the same. To allow direct comparison of the optical switching properties between several films, we utilize the measurement of optical density rather than film thickness. This is because spray-cast polymer films are relatively rough with the measured thickness varying greatly across the films, rendering the determination of average film thickness using conventional metrology methods difficult.[39]

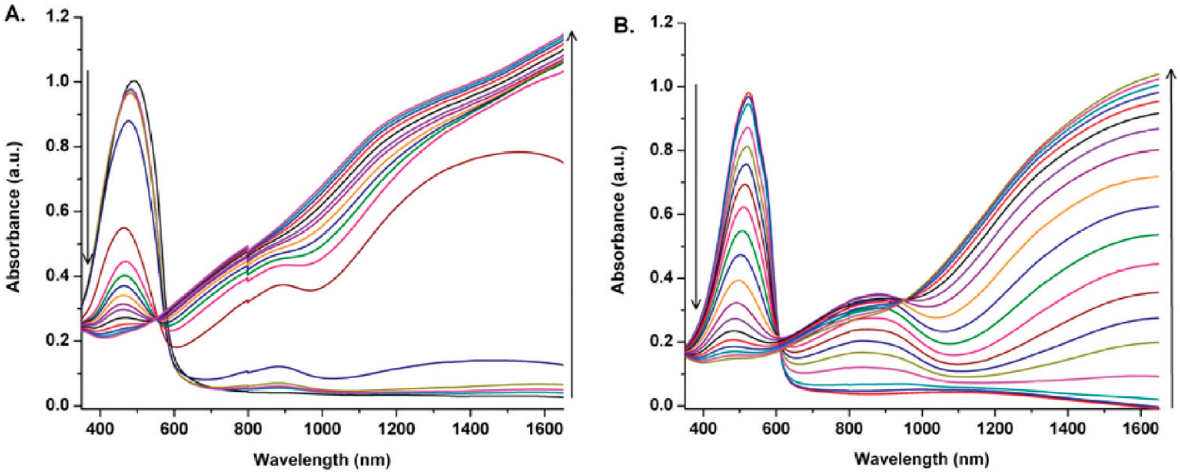


Figure 4. Spectroelectrochemistry of spray-cast films of (A) ECP-orange at the potentials of −0.23, 0.37, 0.38, 0.39, 0.40, 0.41, 0.42, 0.43, 0.44, 0.45, 0.46, 0.47, 0.49, 0.51, 0.53, 0.55, and 0.57 V versus Ag/Ag$^+$ and (B) ECP-red at the potentials of −0.72, −0.22, −0.02, 0.03, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22, 0.24, 0.26, 0.28, 0.30, 0.32, 0.34, and 0.36 V versus Ag/Ag$^+$. Measurements were performed in 0.2 M LiBTI/PC of films spray-cast onto ITO/glass electrodes. The arrow shows the direction of increasing potential.

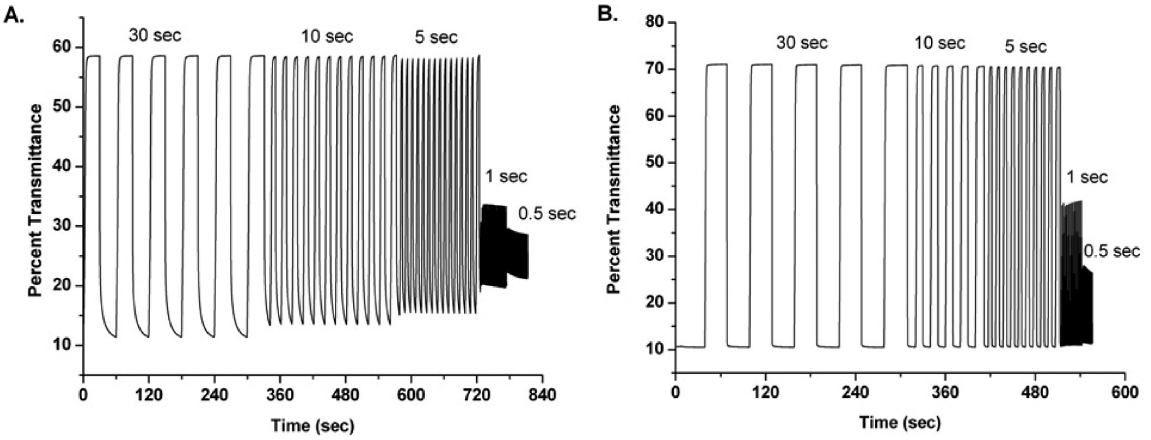


Figure 5. Continuous monitoring of the change in percent transmittance at λ_{max} during switching of (A) a spray-cast film of ECP-orange (with an optical density of 0.98 au) between the potentials of −0.73 and 0.57 V and (B) a spray-cast film of ECP-red (with an optical density of 0.98 au) between the potentials of −0.72 and 0.38 V. All potentials are referenced versus Ag/Ag$^+$ in an electrolyte of 0.2 M LiBTI/PC.

Table 1. Optical Properties (Spectroscopic and Colorimetric) for Films of Increasing Optical Density of ECP-Orange and ECP-Red

polymer	optical density (au)	λ_{max} (nm)[a]	$\Delta\%T$[b]	$\Delta\%Y$[c]	L*a*b* neutral	L*a*b* oxidized	t_{95} (s)[d]
orange	0.59	485	52.1	16.3%	82, 29, 38	90, −2, −3	3.90
	0.98	483	48.2	16.1%	72, 42, 53	81, −2, −7	5.32
	1.2	485	47.4	17.6%	68, 46, 56	80, −3, −9	7.14
red	0.30	529	37.7	27.9%	81, 25, 0	94, −1, 1	1.10
	0.98	525	60.4	41.4%	60, 49, 9	87, −2, 1	2.30
	1.6	523	59.8	38.4%	48, 56, 17	79, −2, 1	4.90

[a] In the fully neutralized state. [b] Difference between steady-state transmittance measured at fully oxidized and fully neutral states. [c] Difference in steady-state relative percent luminance measured at fully oxidized and fully neutral states. [d] Time to reach 95% of full optical contrast between neutralized and fully oxidized states.

An additional factor in switching times is how quickly the polymers can reach a full contrast during steady-state measurements. The steady-state switching speed is typically represented as the time required for the polymer to reach 95% of full contrast when switched from neutral (highly absorptive) to fully oxidized (highly transmissive).[44] The value of 95% is chosen as the human eye is relatively insensitive to the final 5% of a color change with little discerned between 95 and 100% of a full optical contrast. The time to reach 95% of a full optical contrast (t_{95}) when switched from fully neutralized to fully oxidized for films of varying optical density of both ECP-orange and ECP-red is given in Table 1. Not surprisingly, the time required for a film of ECP-orange to reach 95% of a full optical contrast ranges from 1.5 to 3.5 times longer than that for ECP-red, depending on the optical density. We attribute the slower switching speeds and longer t_{95} for ECP-orange, relative to ECP-red, to the more densely packed films for ECP-orange, leading to counterion diffusion in and out of the film to be hindered, slowing the charge balancing of the redox sites within the polymer film.

Colorimetry. Whereas optical spectroscopy measurements of conjugated electroactive polymers convey important information about the electronic transitions and how those change as a function of redox chemistry, they do not yield significant information about the color of the polymer film and how that color is perceived by the human eye.

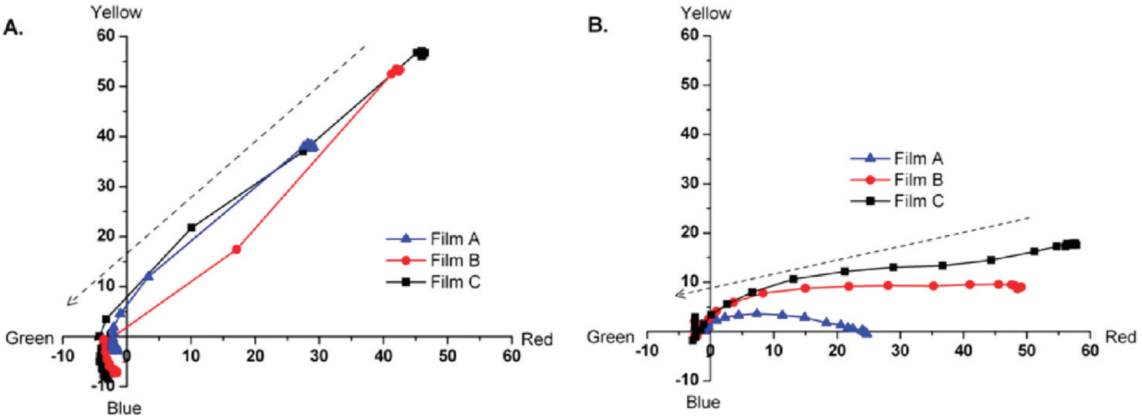


Figure 6. CIE 1976 a*b* values at increasing applied potentials for films of varying optical density of (A) ECP-orange at the potentials of −0.77, −0.27, −0.02, 0.03, 0.08, 0.13, 0.15, 0.17, 0.19, 0.21, 0.23, 0.25, 0.27, 0.29, 0.31, 0.33, 0.35, 0.37, 0.39, 0.41, 0.43, 0.45, 0.47, 0.49, 0.51, and 0.53 V versus Ag/Ag$^+$ (film A = 0.59 au, film B = 0.98 au, and film C = 1.2 au) and (B) ECP-red at the potentials of −0.79, −0.29, −0.19, −0.14, −0.09, −0.07, −0.05, −0.03, −0.01, 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17, 0.19, 0.21, 0.23, 0.25, 0.27, 0.29, and 0.31 V versus Ag/Ag$^+$ (film A = 0.3 au, film B = 0.98 au, and film C = 1.6 au). Measurements were performed in 0.2 M LiBTI/PC of films spray-cast onto ITO/glass electrodes. The arrow shows the direction of increasing potential.

An additional important characterization tool for electrochromic materials is that of colorimetry, where the color of the material is represented quantitatively, allowing for effective comparison of the color of a material as it is switched in addition to comparison between various electrochromic materials.[45−48] While there are many methods to quantify and represent color, one of the most widely applicable to measuring color of materials illuminated by a standard light source is the 1976 CIE LAB (or L*a*b*) with the value of L* representing how light versus dark the measured material is, the value a* representing how red versus green, and b* representing how yellow versus blue the material is, as plotted for several ECPs in Figure 1. In this work, we measured the CIE 1931 Yxy values using a Minolta CS-100 colorimeter as the polymer film is illuminated from behind (transmission measurement method) with a standard D50 light source with the CIE LAB values calculated using methods standardized by CIE.[45,47,48]

The Yxy values are measured in situ as each potential is applied across the polymer film that was spray-cast onto an ITO electrode and immersed in an electrolyte-filled cuvette. From these measurements, the L*, a*, and b* values are calculated for each applied potential. Figure 6A (ECP-orange) and Figure 6B (ECP-red) give the a*b* values plotted for each applied potential for three varied thicknesses (optical density) of polymer film. In addition, the values for fully neutralized and fully oxidized polymer films are given in Table 1. As can be seen in Figure 6A, ECP-orange has a color near equidistant between red and yellow in the neutral state and follows a linear path to the origin of the plot as the polymer becomes oxidized and transmissive. As is expected, the film with the highest optical density has the most saturated color in the neutral state, but a transmissive oxidized state with the highest amount of residual light-blue color, whereas the film with the lowest optical density has the least saturated neutral state and most color-neutral oxidized transmissive state. Similar to the spectroelectrochemistry for ECP-orange, a large color change occurs over a small applied voltage range.

As shown in Figure 6B, the film of ECP-red with the highest optical density has a highly saturated red color in the neutral state but has a slight contribution of yellow when compared with the polymer film with the lowest optical density. As increasing positive potentials are applied to the polymer films, the a* value decreases with both the a* and b* values close to 0 for the fully oxidized polymer, indicating a near colorless transmissive state. As can be seen in Figure 6B and in Table 1, whereas the intensity of red, given by more positive a* values, is higher for the film with the highest optical density and lower for that with the lowest optical density, there is little affect on the oxidized state with all three film having nearly the same near colorless state.

When considering the color of a material, the luminance (lightness or darkness) is also an important measurement given that the measured transmittance is the linear response of a photodetector to changes in the intensity of light, whereas luminance is weighted to the response of the human eye and is therefore more sensitive to perceptions in changes in the brightness of a sample.[48] The percent luminance is most commonly measured relative to a background and given by the relative percent luminance, $\%Y = 100(Y/Y_n)$. The percent luminance measured at each applied potential is plotted for several thicknesses of ECP-orange (Figure 7A) and ECP-red (Figure 7B) in addition to luminance change ($\Delta\%Y$) values in Table 1. It is not unexpected that the $\%Y$ contrast for the polymers is less than the $\%T$ contrast with the change in luminance nearly 1.5 times less than the change in transmittance for ECP-red and nearly three times less for ECP-orange. This can be understood by comparing the spectrum of ECP-red, which peaks at ~525 nm, to that of orange, which peaks at ~484 nm, and how well they overlap with the photopic luminosity function that peaks at 555 nm and is used in the calculation of luminance.[45]

Perspective

The field of conjugated ECPs has seen a growing interest, especially with the availability of commercially available forms of the solution processable PEDOT. However, the availability of fully solution processable polymers exhibiting a variety of colors in the neutral state remains limited. Recent efforts with the introduction of donor−acceptor concepts has made available polymers that switch from blue, turquoise, green, and even black to transmissive with the hue in the neutral state tunable through synthetic methodologies. Much attention has been focused toward the necessity for red, green, and blue materials to allow for additive color displays where the ECP would act as a color filter for a white backlight. If full color displays are desired where the ECP is an active colorant, such as would be in subtractive color displays, then a trichromatic set of polymers of either cyan, magenta, yellow or red, yellow, blue, is necessary. As the palette of colors available for ECPs widens, so does their opportunity for

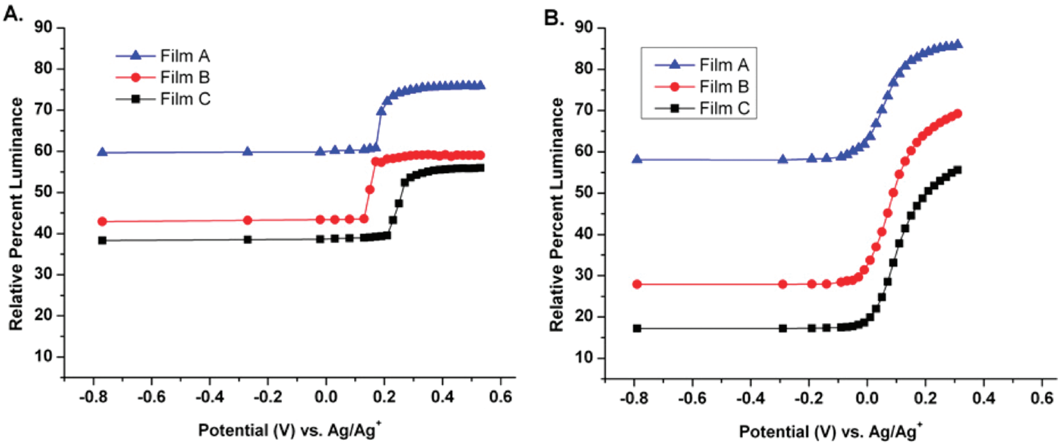


Figure 7. Relative percent luminance as a function of increasing applied potential for (A) ECP-orange (film A = 0.59 au, film B = 0.98 au, film C = 1.2 au) and (B) ECP-red (film A = 0.30 au, film B = 0.98 au, film C = 1.6 au) of spray-cast films on ITO/glass. Measurements were performed in 0.2 M LiBTI/PC.

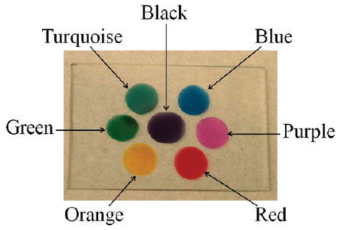


Figure 8. Color wheel of films sequentially spray-cast through a shadow mask of (clockwise from botton right) ECP-red in this manuscript, ECP-orange in this manuscript, ECP-green described in ref 31, ECP-turqoise described in ref 31, ECP-blue described in ref 34, ECP-purple described in ref 27, and ECP-black at the center described in ref 35.

application. Here we extend the color palette of transmissive-switching polymers beyond the green, turquoise, blue, magenta, and black that are available now to polymers that are red and orange, nearly completing the color wheel, as shown in Figure 8.

Experimental Section

Materials and Methods. Lithium bis(trifluoromethane)sulfonimide (LiBTI) (>95%, Fluka) was used as received. PC (anhydrous, 99.7%, Sigma-Aldrich) was used as received and stored under Argon. 3,4-Dimethoxythiophene was purchased from AK Scientific and used as received. ^{1}H NMR spectra were collected on a 300 MHz Varian VXR or a Unity Inova 500 MHz using $CDCl_3$. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with its internal differential refractive index detector (DRI) at 40 °C, using either two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) or a Polymer Laboratories PLgel Mixed-C (5 μm, 300 × 7.5 mm) and a PL mixed-C guard (5 μm, 50 × 7.5 mm) with HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min. Injections were made at 0.05 to 0.07% w/v sample concentration using a 220.5 μL injection volume. Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories, Amherst, MA).

Electrochemistry. Electrochemical measurements were performed using a three-electrode cell with a platinum wire or a Pt flag as the counter electrode, Ag/Ag$^+$ reference electrode, or a silver wire pseudoreference electrode calibrated using a 5 mM solution of Fc/Fc$^+$ in 0.2 M $LiClO_4$ acetonitrile (ACN) electrolyte. The working electrode was either a platinum button (0.02 cm^2) purchased from Bioanalytical Systems or an ITO-coated glass slide (7 × 50 × 0.7 mm, sheet resistance, R_s 8−12 Ω/sq) purchased from Delta Technologies. An EG&G Princeton Applied Research model 273A potentiostat/galvanostat was used under the control of Corrware software. The electrolyte solution was purged with argon before electrochemical measurements performed.

Spectroscopy and Colorimetry. Absorption spectra were performed using a Varian Cary 500 UV−vis/NIR spectrophotometer. In situ colorimetric measurements were performed using a Minolta CS100 colorimeter in transmission mode with a GraphicLite LiteGuard II standard D50 light source. The light source and the sample to be measured were placed in a color viewing booth. The interior of the light booth is coated with a standard gray neutral 8 (GTI Graphic Technology, Inc.) matte latex enamel (equivalent to Munsell N8) to allow for accurate assessment of color of the sample during measurement. Photography was performed in the same light booth using a FujiFilm FinePix S7000 at a shutter speed of 1/160 s, f-stop of f/4, aperture value of f/4.0, ISO of 200, and focal length of 18 mm. The photograph file-type was JPEG, and the files were cropped to only the polymer film to exclude extraneous background using Photoshop. No additional alterations to the files were performed.

Synthesis. *3,4-(2-Ethylhexyloxy)-thiophene*. The synthesis of this monomer was reported previously,[35] and has been modified as follows: In a round-bottomed flask, 3,4-dimethoxythiophene (33.4 g, 0.23 mol), 2-ethylhexanol (80 g, 0.61 mol), and *p*-toulenesulfonic acid monohydrate (4.4 g, 0.023 mol) were combined in toluene (1000 mL). The flask was equipped with a simple distillation head and heated initially to 110 °C. Under a mild flow of nitrogen, the temperature was adjusted to allow for a slow distillation of methanol. The reaction was monitored by TLC. After 7 h, the reaction was allowed to cool. The organics were washed with saturated sodium bicarbonate solution and dried ($MgSO_4$). The solvent was stripped and the residue was distilled, giving the product as a colorless oil: (65 g, 83%) bp 133−35 @ 0.15 mm Hg. δ_H (500 MHz, $CDCl_3$): 6.18 (s, 2H), 3.87 (d, J = 6.0 Hz, 4H), 1.78 (m, 2H), 1.30−1.56 (m, 16H), 0.95 (t, J = 7 Hz, 12H).

Poly{3,4-di(2-ethylhexyloxy)thiophene} (*ECP-Orange*). In a round-bottomed flask, iron(III) chloride (1.43 g, 14.68 mmol) was dissolved in ethyl acetate (10 mL) and stirred under ambient atmosphere. 3,4-Di(2-ethylhexyloxy)thiophene (1 g, 2.94 mmol) was dissolved in ethyl acetate (10 mL) and added to the stirred solution of iron(III) chloride. The reaction mixture immediately turned dark green and was stirred overnight at room temperature. Methanol (80 mL) was added, and the mixture was stirred for 5 min. The doped polymer was collected by suction filtration and washed with methanol (2 × 20 mL). The doped polymer was suspended in chloroform (50 mL), and hydrazine monohydrate (2 mL) was added dropwise, effecting a change in color of the mixture to light-orange/brown, and stirred for 5 min. The mixture was concentrated to ca. 10 mL and precipitated into stirred methanol (100 mL), and the mixture was stirred for 5 min. The polymer was collected, dissolved in chloroform (10 mL), filtered, and reprecipitated into methanol (100 mL). The orange polymer was collected by suction filtration and dried in vacuo. Polymer yield was 0.45 g (45%). GPC (THF vs PS standards): M_w ca. 145−274 kDa, M_n ca. 115−153 kDa, PDI = 1.27 to 1.79; δ_H (300 MHz, $CDCl_3$) 3.92 (br, 4H), 1.77 (br, 2H), 1.56−1.28 (br m, 18H), 0.88 (br, 12H).

Poly{3,4-di(2-ethylhexyloxy)thiophene-co-3,4-di(methoxy)-thiophene} (ECP-Red). Iron(III) chloride (5.73 g, 35.32 mmol) was dissolved in ethyl acetate (20 mL) and stirred under ambient atmosphere. 3,4-Di(2-ethylhexyloxy)thiophene (1.04 g, 3.05 mmol) and 3,4-dimethoxythiophene (0.44 g, 3.05 mmol) were dissolved together in ethyl acetate (10 mL) and added to the stirred solution of iron(III) chloride. The reaction mixture immediately turned dark green and was stirred overnight at room temperature. The mixture was concentrated to ca. 5 mL, methanol (40 mL) was added, and the mixture was stirred for 5 min. The doped polymer was collected by suction filtration and washed with methanol until the washings were clear. The doped polymer was suspended in chloroform (100 mL) and hydrazine monohydrate (2 mL) was added dropwise, effecting a change in color of the mixture to deep red, and the solution was stirred for 5 min. The mixture was concentrated to ca. 20 mL and precipitated into stirred methanol (100 mL), and the mixture was stirred for 5 min. The polymer was collected, dissolved in chloroform (10 mL), filtered, and reprecipitated into methanol (100 mL). The red polymer was collected by suction filtration and dried in vacuo. Polymer yield was 0.31 g (21%). GPC (THF vs PS standards): M_w ca. 35−49 kDa, M_n ca. 11−16 kDa, PDI = 2.12−4.38; δ_H (300 MHz, $CDCl_3$) 3.98 (br, 10H), 2.10−1.20 (br, 18H), 0.89 (br, 12H).

Acknowledgment. We thank BASF for funding and thank Ms. Emily Thompson for technical assistance during the assembly of this manuscript.

Supporting Information Available: Additional electrochemical data including break-in electrochemical scans for ECP-orange, cycling stability for both ECP-orange and ECP-red, and ^{1}H NMR spectra and GPC traces for both polymers This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rosseinsky, D. R.; Mortimer, R. *J. Adv. Mater.* **2001**, *13*, 783.
(2) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*; 1st ed.; Cambridge University Press: Cambridge, U.K., 2007.
(3) Baetens, R.; Jelle, B. P.; Gustavsen, A. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 87.
(4) Granqvist, C. G. *Adv. Sci. Technol.* **2008**, *55*, 205.
(5) Somani, P. R.; Radhakrishnan, S. *Mater. Chem. Phys.* **2003**, *77*, 117.
(6) Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, *27*, 2.
(7) Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. *Adv. Funct. Mater.* **2007**, *17*, 3074.
(8) Dyer, A. L.; Reynolds, J. R. Electrochromism of Conjugated Conducting Polymers. In *Handbook of Conducting Polymers*, 3rd ed.; CRC Press: Boca Raton, FL, 2007; Vol. *1*, Chapter 20.
(9) Granqvist, C. G.; Lansaker, P. C.; Mlyuka, N. R.; Niklasson, G. A.; Avendaño, E. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 2032.
(10) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.
(11) Tshibaka, T.; Ulliel Roche, I.; Dufresne, S.; Lubell, W. D.; Skene, W. G. *J. Org. Chem.* **2009**, *74*, 9497.
(12) Bourgeaux, M.; Skene, W. G. *J. Org. Chem.* **2007**, *72*, 8882.
(13) Dufresne, S.; Bourgeaux, M.; Skene, W. G. *J. Mater. Chem.* **2007**, *17*, 1166.
(14) Galand, E. M.; Mwaura, J. K.; Argun, A. A.; Abboud, K. A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2006**, *39*, 7286.
(15) Irvin, D. J.; Reynolds, J. R. *Polym. Adv. Technol.* **1998**, *9*, 260.
(16) Irvin, J. A.; Schwendeman, I.; Lee, Y.; Abboud, K. A.; Reynolds, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2164.
(17) Sotzing, G. A.; Reddinger, J. L.; Katritzky, A. R.; Soloducho, J.; Musgrave, R.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1997**, *9*, 1578.
(18) Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1121.
(19) Steckler, T. T.; Zhang, X.; Hwang, J.; Honeyager, R.; Ohira, S.; Zhang, X.-H.; Grant, A.; Ellinger, S.; Odom, S. A.; Sweat, D.; Tanner, D. B.; Rinzler, A. G.; Barlow, S.; Bredas, J.-L.; Kippelen, B.; Marder, S. R.; Reynolds, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 2824.
(20) Zhang, X.; Steckler, T. T.; Dasari, R. R.; Ohira, S.; Potscavage, W. J.; Tiwari, S. P.; Coppee, S.; Ellinger, S.; Barlow, S.; Bredas, J.-L.; Kippelen, B.; Reynolds, J. R.; Marder, S. R. *J. Mater. Chem.* **2010**, *20*, 123.
(21) Koyuncu, S.; Zafer, C.; Sefer, E.; Koyuncu, F. B.; Demic, S.; Kaya, I.; Ozdemir, E.; Icli, S. *Synth. Met.* **2009**, *159*, 2013.
(22) Kirchmeyer, S.; Reuter, K. *J. Mater. Chem.* **2005**, *15*, 2077.
(23) Beaupre, S.; Breton, A.-C.; Dumas, J.; Leclerc, M. *Chem. Mater.* **2009**, *21*, 1504.
(24) DuBois, C. J.; Abboud, K. A.; Reynolds, J. R. *J. Phys. Chem. B* **2004**, *108*, 8550.
(25) Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.
(26) Cirpan, A.; Argun, A. A.; Grenier, C. R. G.; Reeves, B. D.; Reynolds, J. R. *J. Mater. Chem.* **2003**, *13*, 2422.
(27) Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559.
(28) Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Funct. Mater.* **2008**, *18*, 2026.
(29) Tarkuc, S.; Udum, Y. A.; Toppare, L. *Polymer* **2009**, *50*, 3458.
(30) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Adv. Mater.* **2008**, *20*, 2772.
(31) Beaujuge, P. M.; Vasilyeva, S. V.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2009**, *42*, 3694.
(32) University of Florida Research Foundation. United States Trademark 77483639, SPRAYDOT, Conjugated Polymer-Based Spray Coating for Coloring and Decorating Electrode Surfaces and Devices, May 27, 2008.
(33) Reeves, B. D.; Unur, E.; Ananthakrishnan, N.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 5344.
(34) Amb, C. M.; Beaujuge, P. M.; Reynolds, J. R. *Adv. Mater.* **2010**, *22*, 724.
(35) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nat. Mater.* **2008**, *7*, 795.
(36) Leclerc, M.; Martinez Diaz, F.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.
(37) Wang, Y.; Lucht, B. L.; Euler, W. B. *Polym. Prepr.* **2002**, *43*, 1160.
(38) Yang, C.; Orfino, F. P.; Holdcroft, S. *Macromolecules* **1996**, *29*, 6510.
(39) Mortimer, R. J.; Graham, K. R.; Grenier, C. R. G.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2269.
(40) Szkurlat, A.; Palys, B.; Mieczkowski, J.; Skompska, M. *Electrochim. Acta* **2003**, *48*, 3665.
(41) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.
(42) Leclerc, M. *Adv. Mater.* **199**, *11*, 1491.
(43) Leclerc, M.; Frechette, M.; Bergeron, J.-Y.; Ranger, M.; Levesque, I.; Faid, K. *Macromol. Chem. Phys.* **1996**, *197*, 2077.
(44) Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3964.
(45) Schanda, J. D. Colorimetry. In *Handbook of Applied Photometry*, DeCusatis, D. C., Ed.; Optical Society of America: New York, 1998.
(46) Wyszecki, G.; Stiles, W. S. *Color Science: Concepts and Methods, Quantitative Data and Formulae*, 2nd ed.; John Wiley and Sons, Inc: New York, 1982.
(47) CIE Publ. No. 15.2. *Colorimetry*, **1986**.
(48) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563.