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Navigating the Color Palette of Solution-Processable Electrochromic Polymers[†]

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Solution-processable electrochromic (EC) polymers that can be switched from one distinct color state to a highly transmissive and near colorless state are required for applications in both EC windows and displays. Using a tour around the color wheel, we describe the various EC polymer (ECP) compositions that now make a full palette of colors available demonstrating a set of structure−property relationships. Electrochemical and electrochromic characterization methodologies are described and their application to ECPs demonstrated. Processing and patterning methods including spray casting, screen-, flexo-, and ink jet printing, along with photo- and soft lithography are described. Absorptive/transmissive (window type) and absorptive/reflective (display type) devices are described as platforms for practical applications.

Introduction

The creation of solution-processable π-conjugated polymers, whether prepared through a soluble precursor route or directly by the introduction of flexible substituents onto the polymer main chain, has led to a revolution in their applicability in a myriad of applications.[1] This field was stimulated by early work developing regioregular poly(3-alkylthiophenes) (rr-P3AT) where especially high conductivities were attained with highly ordered structures prepared by solution deposition, followed by oxidative doping.[2,3] This was followed by poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) as a stable aqueous dispersion that could be processed to thin films with high conductivity (low surface resistivity) along with a concomitant high degree of transmissivity throughout the visible region of the spectrum.[4,5] These transmissive and conducting films have proven useful in a number of optoelectronic devices and PEDOT/PSS has become the most useful of the commercially available conducting polymers because of its combination of optical properties, stability, and processability.

Charge neutral solution processable conjugated polymers have proven to exhibit a number of potentially useful semiconducting properties. This is illustrated by poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV), which was shown to be an excellent light emitter useful for the construction of polymer light emitting diodes (PLEDs).[6] More recently, the semiconducting charge transport properties have allowed field effect transistors (FETs) to be constructed where mobilities greater than 1 $cm^2\ V^{-1}\ s^{-1}$ have been measured.[7,8] In this instance, it is the combined ability of the side chains to induce ordered interactions between the polymer chains, in addition to their solution processability, that leads to the highest performance materials. Solution-processable π-conjugated polymers have also found significant application in polymer photodetectors[9] and solar cells.[10−12] Applicable to both bilayer and bulk heterojunction (BHJ) cell configurations, the solubilizing side chains play an important role in controlling the morphology of the films prepared and their ability to interact with blending components, such as fullerenes, which serve as electron accepting species to the electron-donating polymers. Without the solution processability noted for each case above, the performance of these materials and possibilities for real applications would be limited.

In this contribution, we focus on soluble π-conjugated polymers in which redox activity is required for their use. Possible applications for these types of polymers span charge storage (batteries and supercapacitors),[13] chem-[14] and biosensors[15], and electrochemically induced actuators.[16] Specifically, we focus on how redox switchable polymers can undergo a concurrent optical change that leads to an electrochromic (EC) response from the materials. The EC effect has been known for quite some time and great strides have been made with metal oxides (e.g., WO_3), molecular organic electrochromes (e.g., viologen derivatives), and electrodeposited π-conjugated polymers films.[17] In this field, if one is to capture the true utility of organic polymers, again processability is the key. Here, we focus on solution-processable electrochromic polymers (ECPs) where the backbone structure leads to fine control of the optical properties, and the side chains allow optimization of the solution processability. There has been a significant body of work published and reviewed on ECPs,[18−20] often where the focus has been

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on their multicolored nature, in essence where the polymer switches between two or more different color states. These types of polymers are exemplified by the P3ATs (switching red to blue), polypyrrole (switching yellow to black), and polyaniline (switching from yellow through green, blue, and violet) along with countless other derivatives (many based on dioxythiophene repeat units) where essentially every color of the spectrum has been attained. Although the spectral control attained as a function of structure teaches much about their π electronic properties, these systems tend to serve as scientific curiosities; none of them have reached practical utility as electrochromes as the switching between two distinct and highly colored states is not especially useful.

Electrochemically prepared films of PEDOT, along with PEDOT/PSS, were the first ECP systems to provide a strong deep color in one state (deep blue) that could be repeatedly and stably switched to a highly transmissive and near transparent state.[21-24] This phenomenon is especially important when considering the use of ECPs in window-type and display-type devices as each requires a distinct colored and a highly transmissive form for these applications to be successful. A further benefit when considering ECPs, such as PEDOT/PSS, in these applications is that they are bistable in terms of the setting of their redox states electrochemically. Introduction of an appropriate oxidizing or reducing potential passes charge through the ECP, thus setting it in the charged state (and one color state) of choice. Removal of the applied potential to open circuit then yields a stable system in that color state, possibly where only a small electrochemical refresh is occasionally required to retain the fully transmissive or vibrantly colored state.

The ability of the synthetic polymer chemist to develop electron rich π-conjugated polymers (those with high HOMO values) make them easy to oxidize and to subsequently be charge neutralized, giving low oxidation potentials as needed for high device stabilities where the system is driven between its two extreme states repeatedly. By controlling the magnitude of the HOMO−LUMO gap (often termed the band gap) the wavelength maximum for absorption by π-conjugated polymers can be tuned from the ultraviolet, through the entire visible region of the spectrum, and well into the near-infrared. As such, a spectrum of colors is accessible using a single band of absorbance, thus transmitting or reflecting the observed color. In some systems, such as those materials that transmit or reflect green light, a simultaneous two-band absorption of the red and the blue portions of the spectrum are required.[25-27] This has been attained using donor−acceptor (DA) systems that have proven useful in synthesizing a number of colored to transmissive switching ECPs, including those that switch from deep black to highly transmissive.[28]

With these above considerations, this contribution details how the repeat unit structure of solution processable π-conjugated polymers can be varied to provide ECPs of essentially any color that switch to highly transmissive. We address the interplay of the nature of the electron-rich and electron-poor moieties used along the backbone, in addition to the chemical nature of the side chains employed. These can span from nonpolar for solubility in typical organic solvents, polar and ionic for solubility in polar solvents and water, and reactive substituents in which the solubility can be changed based on the chemical state of the side chain.[29] Using these chemistries, a continuous change in the absorption profiles (leading to careful control of color and optical density) yields a set of materials with a near full color palette, all able to switch to the transmissive state. The characterization of the electrochemical, spectroscopic, and colorimetric properties of these polymers is then discussed in order to allow the reader to understand how these structure−property relationships are logically developed. Finally, we utilize a set of absorptive/transmissive (window-type) and reflective (display-type) electrochromic device (ECD) platforms as means for the characterization of the ECPs which also serve as demonstrations for their potential utility in real world applications.

Navigating the Color Palette

Cathodically Coloring Polymers. When designing polymers with specific colors in mind, one can refer to the immense literature base on how molecular structure relates to absorption in the visible region of the spectrum. However, especially for the uninitiated scientist, the relationship between the visible absorption spectrum for a material and its observed color is not always obvious. The colors we see for any given material are a product of the light reflected and/or transmitted by the object, but the nonlinear sensitivity of the human eye to different wavelengths of light must also be considered. As such, the simple system of complementary (or opposite) colors easily allows one to relate the maximum color absorbed to the color perceived in many cases. For example, materials that are yellow in color do not have an absorption minimum in the yellow part of the spectrum (560−600 nm), but rather have maximum absorption in the violet (400−440 nm) region of the spectrum, as violet is yellow's complementary color. Accordingly, the absorption of complementary colors can often yield the yellow, orange, red, purple, and blue materials.

Unfortunately, the simple model of absorbing complementary colors is insufficient when considering the color green, since green's complementary color is red, and a maximum absorption in the red region of the spectrum does not necessarily mean that green will be observed. In reality, two absorption bands are needed—one in the red region of the spectrum, and one in the blue-violet region, to give an absorption trough in the green region of the spectrum. If significant red absorption is present, the color observed will depend on the position of the valley in the absorption spectrum, which can give colors from saturated blue, to blue-green hues, to saturated greens. Fortuitously, the donor−acceptor approach typically yields polymers with two distinct absorption bands, both of which can be tuned to give the colors green, blue-green, and blue.[27,28,30-33]

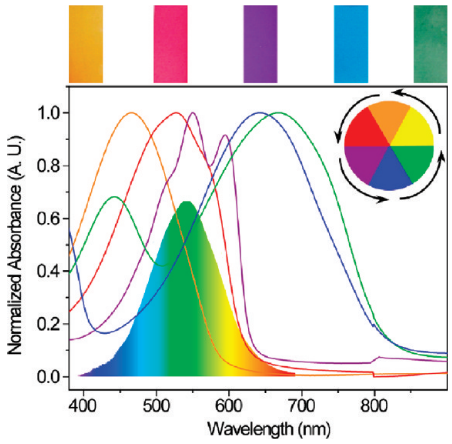


Figure 1. Visible absorption spectra of orange, red, purple, green, and blue polymers, with the inset curve of sensitivity of the human eye relative to wavelength, and color wheel in upper right. Photographs of the materials on ITO-coated glass are shown above.

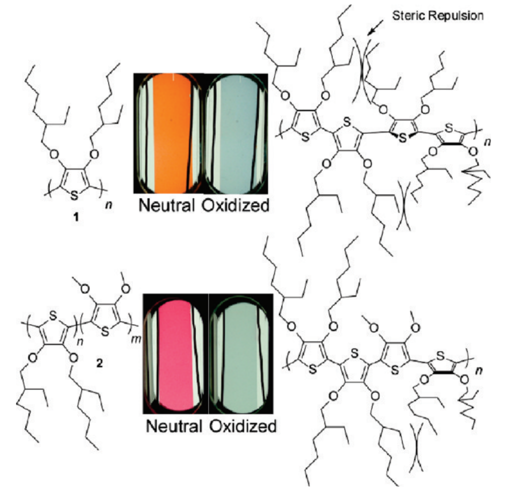
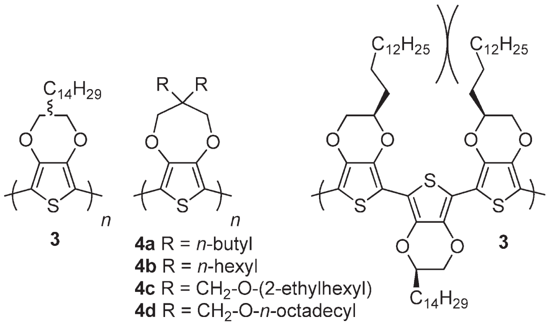


Figure 2. Repeat unit structures of orange and red-to-transmissive conjugated polymers, showing steric repulsions between side chains and backbone twisting. Photographs are of the polymers switched from their neutral colored and oxidized transmissive states.



4a R = *n*-butyl
4b R = *n*-hexyl
4c R = CH_2-O-(2-ethylhexyl)
4d R = CH_2-O-*n*-octadecyl

Figure 3. Solution-processable purple-to-transmissive conjugated polymers and possible steric repulsions between side chains in PEDOT-C14 (**3**).

To demonstrate the concepts that relate the absorption spectrum of a material to its observed color, Figure 1 shows the visible absorption spectra of orange, red, purple, blue, and green conjugated polymers, along with photographs of films (top), the relative sensitivities of each color to the eye (bottom), and a color wheel showing complementary colors. The figure shows that the maximum absorption of the orange, red, and purple polymers (long wavelength band) lies on the color complementary to it on the color wheel. In the next section, the examples of each color of cathodically coloring EC polymers are discussed, focusing on color tuning through structure—function relationships. As anodically coloring polymers generally switch from a colorless neutral state to colored doped states, oftentimes going through many different colors at various potentials, they will be discussed in a separate section.

Because dioxythiophenes are a principal heterocycle in almost all cathodically coloring ECPs, a thorough understanding of steric and electronic effects in these systems is quite important for color tuning. We have recently observed that changes in the alkylene groups of the dioxythiophenes, from EDOT to ProDOT, to open chain dioxythiophenes, gives little change in the peak oxidation potential of the hydrogen terminated monomer units. Consequently, we believe that the substitution pattern beyond the oxygen atoms has little affect on the electronics of the individual heterocycles. Therefore, it is more likely steric interactions between repeat units that tune the color states of dioxythiophene-based polymers by limiting the effective conjugation lengths. With this in mind, we will discuss the relationships between polymer structure and observed color in the following sections, using the color wheel in Figure 1 as a guide.

Orange and Red. Beginning our journey around the color wheel, we discuss the colors orange and red. In general, cathodically coloring orange- or red-to-transmissive switching polymers are uncommon, as the high bandgap required to yield these colors makes shifting the bipolaronic transition fully into the NIR after oxidation quite difficult. This has recently been overcome with the use of open-chain dioxythiophene polymers shown in Figure 2, as reported by Dyer et al.[34]

The acyclic side chains of the dioxythiophenes shown in Figure 2, cause steric repulsions that decrease the effective conjugation length in the orange homopolymer (**1**), giving rise to a moderately high band gap (2.04 eV) and absorption maximum at 483 nm. The random incorporation of dimethoxythiophene units into the backbone (**2**) relaxes the steric repulsions, lowering the band gap slightly (2.00 eV), but shifting the $\lambda_{\max}$ significantly to 525 nm, yielding a red colored material. Both polymers are able to bleach quite effectively, giving contrast ratios as high as 48% for orange and 60% for red, measured at the $\lambda_{\max}$ of each respective polymer. Shown in Figure 2 are repeat unit structures for both the red and orange polymers showing possible steric interactions between pendant chains.

Purple and Magenta. Rotating counter-clockwise around the color wheel in Figure 1, we come to the colors magenta and purple. The structure of the first solution processable cathodically coloring electrochromic polymer, a purple colored tetradecyl substituted derivative of PEDOT (**3**), is shown in Figure 3. The polymer was first reported by Kumar and Reynolds in 1996,[35] and was synthesized by oxidation of the corresponding monomeric heterocycle with $FeCl_3$, giving polymers with M_n up to 8200 Da. The material could be both doped by oxidation in solution, or airbrush cast films doped either chemically or electrochemically, switching from dark purple (E_g = 1.78 eV) to a transmissive faint green color state. A contrast ratio of 54% can be calculated from the spectroelectrochemical data yielding a value comparable with the electropolymerized polymer (60%).[36,37] Interestingly, drop-cast films could not switch as effectively as spray-cast films, as the more compact morphology of these types of polymers did not allow complete electrochemical oxidation. This trend seems to be general for EC polymers, as most materials that achieve high contrasts are either electropolymerized or spray-cast.

Interestingly, the color of **3** does not match the color of unsubstituted PEDOT. A possible explanation for this is illustrated by the sketch on the right in Figure 3, which shows possible repulsive steric interactions between repeats. The regiorandom and atactic nature of the solubilizing side chains induce significant repulsion between repeats, reducing backbone planarity and limiting effective conjugation length in the neutral state. Additionally, those interactions decrease ordering and π-stacking interactions in the solid state, also causing a hypsochromic shift in absorption when compared to unsubstituted PEDOT. As such, the band gap of the soluble derivative is not low enough to absorb much of the red region of the spectrum, and thus the film appears purple; whereas PEDOT with its lower band gap (1.60 eV)[4] effectively absorbs long wavelengths and appears blue to the eye.

A further development in processable EC polymers occurred in 2002, when propylenedioxythiophene (ProDOT) moieties functionalized with butyl (**4a**)[38] side chains were synthesized using Grignard Metathesis polymerization (GriM)[39] to yield a soluble low molecular weight (M_n ~6000) polymer that was solution cast and redox switched on ITO-coated glass between dark purple and transmissive/sky blue states. Since the higher molecular weight fractions of polymer were insoluble, PProDOTs with longer side chains such as hexyl (**4b**), ethylhexyloxy (**4c**), and *n*-octadecyloxy (**4d**) were investigated and reported in 2003–2004, with the intent to improve film-forming qualities.[40,41] The resulting polymers gave fairly high molecular weights (> 30 000 Da) and displayed sufficient solubility in organic solvents such as THF, toluene, and chloroform for processing. Through this study, it was discovered that the 2-ethylhexyloxy side group gave the best combination of high contrast ratio (80%) and switching rate (95% of a full switch in 0.6 s) when compared to all other solubilizing groups studied. It has been rationalized that the branched side chain gives an "open" morphology, allowing dopant ions to be quickly transported through the films. A spray cast film of **4c** is shown on the left of Figure 4, where a reddish hue is apparent immediately after deposition. Upon oxidation, the polymer switches to a highly transmissive state (center), and then reversibly switches between the more purple hue on the right and the highly transmissive state. It is believed that "electrochemical annealing" causes the slight red shift in absorption, because of a higher degree of ordering upon redox cycling.

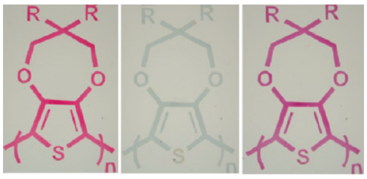


Figure 4. Photographs of a film of **4c** on ITO-coated glass: left, as cast; center, the same film at 0.95 V vs Ag wire QRE (switched in 0.1 M tetrabutylammonium hexafluorophosphate in propylene carbonate); right, the film after electrochemical switching held at −0.35 V vs Ag wire QRE.

Blue. Continuing around the color wheel, we come to the color blue, which requires a maximum absorption in the orange and red region of the spectrum, with significant absorption at the farthest red wavelengths of the visible. Most of the light transmitted is blue and violet, and because the eye is more sensitive to blue, that is the color observed. The low band gap required to achieve blue materials makes the synthesis of soluble dioxythiophene-based homopolymers challenging, but a fair number of effective nonprocessable blue EC materials have been produced by electropolymerization.[42,43] Some of these materials have reached up to 90% contrast ratio in the visible, an impressive value.[44,45]

The original blue-to-transmissive electrochromic polymer, PEDOT, has been solution processed as an aqueous dispersion, PEDOT/PSS, to fabricate large area EC windows, using spin coating or doctor blading as the deposition technique.[22] The 30 cm × 30 cm window was shown to switch between dark blue and a transmissive light blue. With such a simple and available material, one may ask, why is there any reason to develop new blue EC polymers. Our motivation has been to attain a full family of compatible materials that are spray-processable from organic solvents.

As functionalization of PEDOT with solubilizing side groups results in a hypsochromic shift in absorption, the donor–acceptor approach has been employed successfully to yield blue polymers. This started with the work of Thompson et al. on cyanovinylene/dioxythiophene containing polymers shown in Figure 5 (**5**), which were functional as both solar cell materials and electrochromics.[46] Here, a cyanovinylene acceptor unit was employed to red-shift the absorption with respect to PProDOT homopolymers to give maximum absorption from 610 to 620 nm. The best electrochromic polymer in the series, **5**, gave approximately a 40% contrast ratio at the neutral state λ_{max}. Amb et al. also reported a series of blue-to-transmissive switching copolymers (**6a**–**6c**) consisting of alternating ProDOT and 2,1,3-benzothiadiazole (BTD) heterocycles, which were synthesized by Suzuki methodology giving contrast ratios up to 52%, and subsecond switching speeds.[30] In this case, the solubility of the polymer film could be modified using ester functionalized side groups (**6c**) that could be cleaved in a

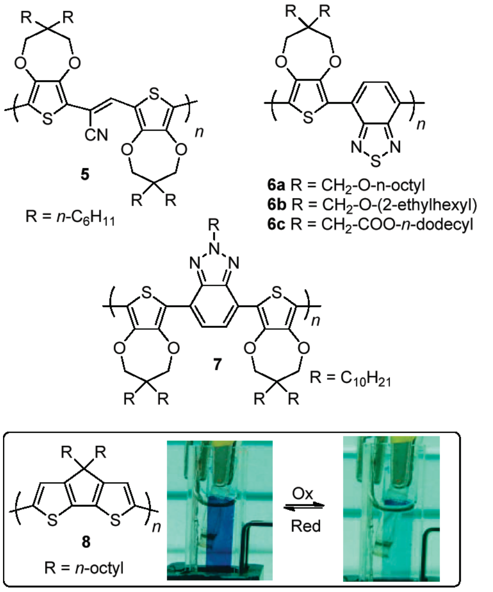


Figure 5. Solution-processable blue-to-transmissive conjugated polymers, with photographs of the blue and transmissive states of PCPDT, (**8**). Reproduced with permission from ref 47. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

post-deposition saponification. The study reinforced the theory that a reduction in the ratio of donor-to-acceptor heterocycles in conjugated polymers shifts the high energy absorption band to shorter wavelength,[28] in this case shifting it entirely into the UV. Recently, Icli et al.[31] have also produced a blue EC polymer, by incorporating a benzotriazole unit into a ProDOT backbone. The benzotriazole ring acts as a weaker acceptor than commonly used benzothiadiazole and thus allows a slight bathochromic shift in absorption when compared to BTD-containing analogues, here shifting the color from blue-green to saturated blue. Spray coated films of the polymer achieved useful contrast ratios of up to 43% at 560 nm, with the same polymer produced electrochemically giving up to 61% contrast.

Though in general soluble dioxythiophene homopolymers do not yield blue polymers due to their lack of absorption in the far red, some homopolymeric species of other heterocycles have been shown to yield blue electrochromes. The bottom of Figure 5 shows the structure and photographs of poly(4,4-dioctyl-cyclopenta[2,1-b:3,4-b′]-dithiophene (**8**) in neutral and oxidized states. This polymer has been shown to be an excellent soluble electrochrome, giving up to 60% contrast, subsecond switching times, and high coloration efficiencies (up to 923 cm^2/C).[47] The cyclopentadithiophene (CPDT) ring extends the effective conjugation length through both ring fusion and prohibition of steric repulsions of the side chains, thus decreasing its band gap with respect to P3HT. The quaternary carbon bridge on CPDT may also play a role in allowing the high electrochemical doping levels required to fully transfer the visible absorption bands into the NIR upon oxidation, by discouraging close π-stacking interactions in the solid state[48] and possibly allowing dopant ions to easily penetrate the film.

Turquoise and Green. Moving further around the color wheel, we come to the color green, and this section will encompass both green and intermediate blue-green hues. As stated previously, dual absorption bands are required to yield a green color; one band absorbing the blue-violet portion of the spectrum, and the other absorbing red, to give a window of transmission in the green region of the spectrum. A drive to produce the color green pointed out in the literature is the concept of RGB complementary colors to give EC devices that can give any color. It should be clarified that this is true only when emissive light sources are utilized, because red, green and blue are additive primary colors, whereas red, yellow, and blue or cyan, magenta, and yellow are subtractive primary colors. Only combinations of these subtractive primaries in an absorptive/transmissive or absorptive/reflective EC device can give close to all colors.

As it has been shown that the wavelength and intensity of the high energy absorption band in donor−acceptor polymers is dependent on the character of the donor moiety and its relative ratio of donor-to-acceptor along the backbone,[28] green EC polymers have generally been achieved through copolymers consisting of runs of dioxythiophene segments, with intermittent acceptors such as BTD. Other approaches involve the use of heterocycles that favor quinoidal type bonding such as thienopyrazine, or the copolymerization of dioxythiophenes with stronger acceptors such as benzoselenadiazole. Presumably, strong donor−acceptor interactions play a role in forcing both absorption bands into the visible region, leaving a window of transmission in the green region of the spectrum.

Although one of the oldest known conjugated polymers, polyaniline (emeraldine form) displays a dark green color,[49] green has historically been difficult to achieve in other EC polymers. The first report of a green electrochromic polymer to our knowledge came in 2002, when Dubois and Reynolds reported a green to gray switching electrochromic polymer that consisted of alternating units of bi-EDOT and pyrido[3,4-*b*]pyrazine segments.[50] Subsequently in 2004, the Wudl group[25,32] reported a soluble bithiophene-thienopyrazine copolymer **9** (Figure 6) that also gave the necessary two band absorption with a transmission window in the absorption spectrum at 550 nm. However, the significant residual color of the oxidized states of both polymers left room for improvements to be made.

Following this work, in 2008 Beaujuge et al. developed the first series of solution processable green-to-transmissive polymers using the donor−acceptor approach, and the structures of the polymers are shown in Figure 6 (**10**−**12**).[27,28] Consisting of blocks of electron-rich heterocycles spaced by BTD, **10** and **11** exhibited electrochromic contrasts of up to 53% at the long wavelength absorption maxima. The films also lost as little as 4% of their contrast ratio when the switch time was decreased from 10 to 1 s, thus showing promise for the materials to be used in display type devices.

In another work, the role of unsaturated alkene or alkyne linkages between heterocycles was evaluated, and

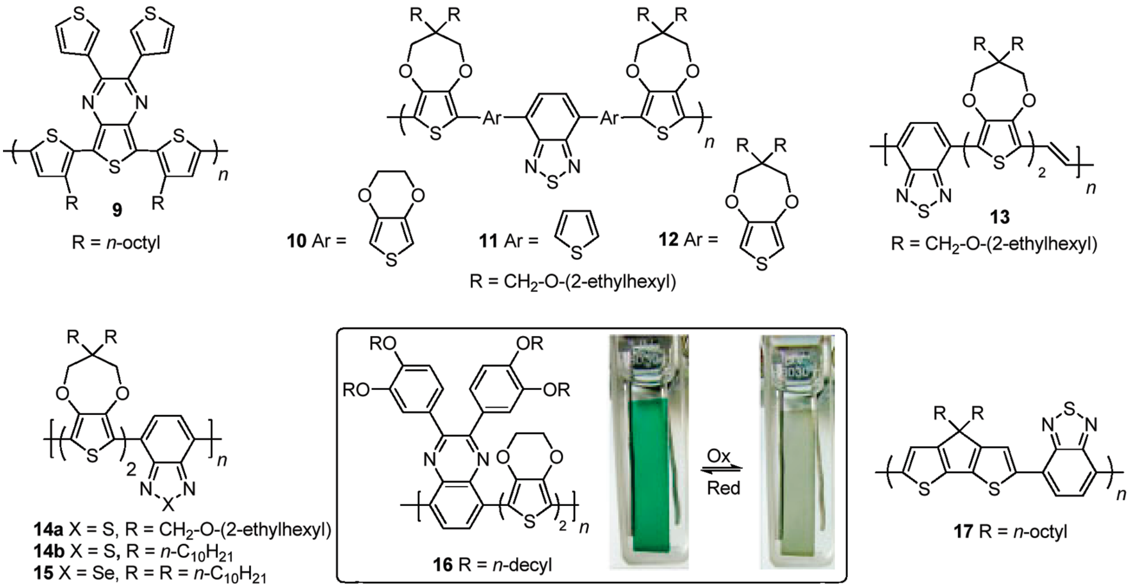


Figure 6. Soluble green electrochromic polymers, with photographs of **16** in neutral and oxidized states. Reproduced with permission from ref 33. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

more green-to-transmissive polymers were produced.[51] Here, an alkene spaced polymer **13** (Figure 6) gave a red shift in absorption with respect to the parent polymer **14a**, resulting in a shift in color from turquoise to green. Both **13** and **14a** gave transmissive states upon oxidation, whereas analogues of **13** containing alkyne linkages were unable to effectively bleach and did not result in a bathochromic shift in absorption. The reason for the inability to bleach was attributed to the inability of the alkyne linked polymers to form well-defined bipolaronic transitions in the NIR.

In a recent report from Içli et al., the effect of changing the acceptor moiety from the most commonly used BTD to benzoselenadiazole (BSD) and benzotriazole in biProDOT containing polymers was studied, and it was shown that the color could also be modulated as a function of acceptor strength.[31,52] The highly electron deficient BSD in polymer **15** caused a red shift in the absorption when compared to its BTD analogue **14b**, resulting in a shift in color from turquoise to saturated green. This polymer bleached effectively upon oxidation to give a contrast ratio of 42% at 732 nm, and also displayed subsecond switching times.

In addition to the Reynolds and Wudl groups, the Toppare group produced the processable green-to-transmissive polymer **16** (Figure 6), by oxidative polymerization of a bis-EDOT-quinoxaline trimer. The vibrantly green polymer was spray-processed and switched with up to 42% contrast at the long wavelength absorption maximum, and achieved 95% of a full switch in less than 1 s.[33] Photographs of spray-cast films of the polymer in its neutral and oxidized states are also shown in Figure 6.

In another work, Wu et al. reported a green- to-transmissive polymer based on cyclopentadithiophene (CPDT) as the donor in the alternating CPDT-BTD copolymer **17**. The polymer gave a green neutral state that bleached to a light blue transmissive state with maximum optical contrast of 38%.[52]

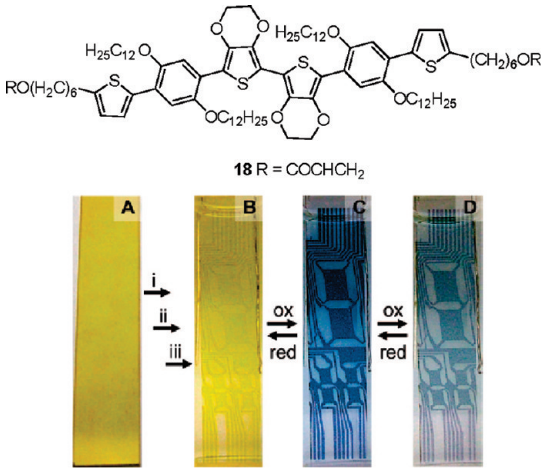


Figure 7. Top: structure of telechelic oligomer. Bottom: Photographs of spray cast films of the oligomer. (A) Pristine and (B) after UV irradiation through a shadow mask and washing with THF; (C) oxidation to cationic state; (D) further oxidation to dicationic near transmissive state. Reproduced with permission from ref 53. Copyright 2008 American Chemical Society.

Yellow. Further circling the color wheel, we come to yellow. No cathodically coloring yellow polymers have yet been reported in the literature to our knowledge. The high band gap required to produce yellow materials makes it difficult to attain effective transfer of the absorption bands to the NIR after oxidation for these materials. Importantly, yellow-to-transmissive polymers are needed as yellow fulfills both sets of subtractive complementary colors, red-yellow-blue and cyan-magenta-yellow. Although no examples of cathodically coloring yellow polymers have yet been published, there are a few examples of yellow-to-transmissive anodically coloring polymers, which will be highlighted in the corresponding section.

A system that nearly displays yellow-to-transmissive behavior was reported by Nielsen et al.,[53] where a yellow telechelic oligomer **18** (shown in Figure 7) was spray-cast

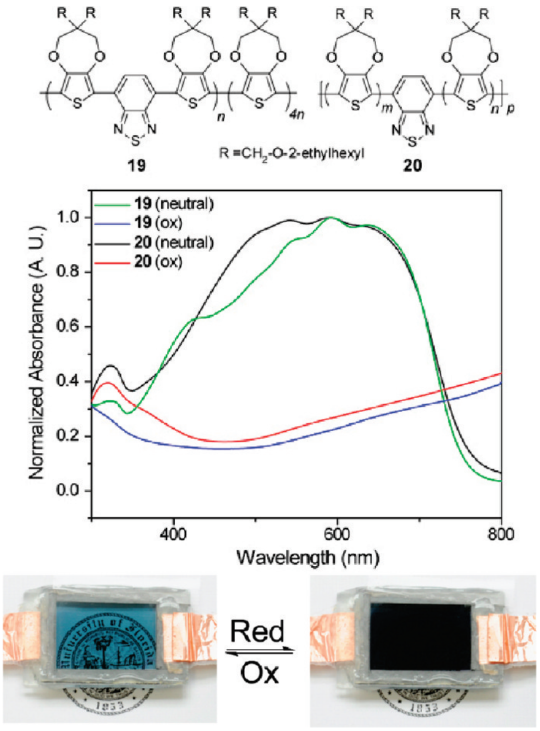


Figure 8. Structures of black to transmissive ECPs (above) and absorption spectra of the polymers in their neutral and oxidized states. The absorbance of the two neutral spectra were normalized, and the same correction factor was applied to each of the respective oxidized states. The bottom shows a black-to-transmissive switching device. Reproduced with permission from ref 55. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

onto ITO, and patterns were created via UV promoted acrylate polymerization through a shadow mask. Here, the neutral yellow films were oxidized to their dark blue monocation, and finally to their faint blue/gray dication.

Black. The color black is achieved by uniform absorption of all visible wavelengths of light, and as such synthesis of conjugated polymers that absorb the entire spectrum evenly, and can be fully bleached upon oxidation, has been a difficult affair. Through the use of two or more different polymers, black EC devices were achieved; however, in the ideal case, one material would absorb the entire spectrum.[54] Indeed, in order to obtain a black conjugated polymer, it seems that several chromophores must be at work simultaneously in order to give this broad and uniform absorption.

The first black-to-transmissive ECP was reported by Beaujuge et al., and showed that random copolymerization of two discrete monomer units can give a black neutral state polymer, and the structure is shown in Figure 8a (**19**).[28] In this systematic study, the ratio of donor ProDOT, or branched alkoxythiophene moieties, to BTD was modulated by synthesizing discrete oligomers and oxidatively polymerizing them. It was shown that the ratio of electron-rich to electron-poor heterocycles in the main chain controlled the energy and intensity of the short-wavelength absorption band, with more donor moiety giving the most intense and red-shifted high energy band. The study culminated with the random copolymerization of a ProDOT-BTD-ProDOT oligomer with ProDOT in 1:4 molar ratio, giving a material that absorbs broadly over the entire spectrum. The polymer was then spray-cast onto ITO, and electrochemical oxidation revealed a near-colorless oxidized state, with a maximum 52% contrast ratio at 592 nm.

In subsequent work, the breadth and uniformity of absorption of ProDOT-BTD containing black polymers was improved by utilizing Stille polymerization[55] to give polymer **20** (where $m + n = 7$) and a comparison of the visible absorption spectra of both polymers is shown in Figure 8. It is evident that the polymer produced by the Stille method more effectively absorbs the high energy part of the spectrum, likely due to the higher degree of randomness possible with the polymerization method. In the improved Stille method, dibromo- and distannyl-substituted ProDOTs were copolymerized with dibromo-BTD, using palladium catalysis. In the method of Beaujuge et al., oxidative polymerization was used where there must be at least 2 ProDOTs between BTD units, whereas with the Stille method it is possible to have segments with only one ProDOT between each acceptor.

Only one other report of black-to-transmissive polymers has come since this work to the best of our knowledge, a random copolymer system that combines the trimeric precursors of polymers **7** (Figure 5) and **15** (Figure 6) in an oxidative polymerization to give black soluble materials.[56] More work needs to be done on this promising system, however, as their low contrast (15% at 522 nm) is quite surprising considering the higher contrasts of the two polymer components.

Anodically Coloring Polymers. Anodically coloring polymers bring forth a different set of advantages and challenges when compared to the cathodically coloring materials discussed in the previous sections. Here, a high degree of transmissivity is fairly easy to accomplish, since the high band gap (absorption fully in the UV) of these types of polymers can render them almost completely transparent in their neutral state as evident for various compositions of poly(*p*-phenylene).[57] However, attaining the high HOMO levels required for repeated and stable redox reactions requires electron rich monomers as best exemplified by the *N*-alkyl derivatives of the poly(3,4-alkylenedioxypyrrole) (PProDOP) family.[58] In most systems that have been recently reported, the triarylamine functionality is utilized as these systems generally give high band gaps, high HOMO levels, and colored radical cations upon oxidation. Groups linking these functionalities are generally cross-conjugated systems, or amide groups, which serves to limit conjugation in the neutral state to avoid visible absorption.

Color control in the oxidized state of anodically coloring polymers is difficult to attain, and oftentimes different color states with poor saturation appear at different biases. Therefore, we consider these polymers beyond the scope of this review, and we will not discuss them in detail with the exception of those that can access the color yellow, the color least accessible for cathodically coloring polymers.

Importantly, transmissive-to-yellow polymers of this class do exist, and an example is polymer **21** (shown in

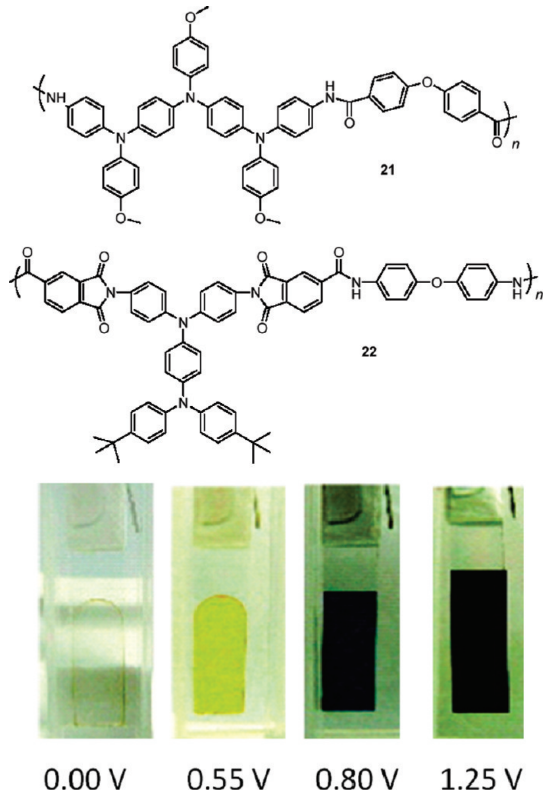


Figure 9. Structure of anodically coloring transmissive-to-yellow polymers **21** (top) and **22** (bottom), and photographs of films of **21** at various potentials vs Ag/AgCl. Adapted with permission from ref 59. Copyright 2008 American Chemical Society.

Figure 9),[59] along with photographs of films of this material at various voltages. The polymer switches from transparent at 0 V vs Ag/AgCl, to yellow at 0.55 V. Upon cycling to higher potentials, another film switched to blue at 0.80 V, to black at 1.2 V. The polymer exhibited a contrast of 59% at 443 nm, and required 2.2 s to reach 90% coloration, whereas it decolored in less than 1 s. Recently, Wang et al.[60] reported another series of polyamides including polymer **22** which also switched between a transparent neutral state and a yellow state at intermediate potentials. In this study, contrasts of ~50% at 411 nm could be estimated from spectroelectrochemical data. Films were electrochemically oxidized at 0.7−0.9 V vs Ag/AgCl, and at higher potentials the films accessed blue and green color states.

Film Characterization

While full electrochromic characterization of these materials is paramount in allowing a fundamental understanding of their optoelectronic properties, providing a means for direct comparison among newly synthesized materials, and forecasting for how these properties would extend to final device performance, what characterizations are performed and how they are interpreted is widely inconsistent across the field. Here, we provide a brief overview of the potentially useful methods as applied to thin films of solution processable electrochromic polymers.

Electrochemistry. Electrochemical characterization is one of the most important characterization methods employed for electrochromic polymers, and yet one of the least understood.[17,61−63] The most commonly used experimental method for probing the redox properties of surface confined electroactive polymer films is cyclic voltammetry (CV). As shown in Figure 10, for a well-behaved ECP, the redox peaks for oxidation ($E_{p,ox}$) and reneutralization ($E_{p,red}$) are resolved such that a half-wave potential ($E_{1/2}$), lies midway between the two peak potentials and can be determined by $E_{1/2} = (E_{p,ox} + E_{p,red})/2$ as shown in Figure 10A for polymer **2**. Additionally, oxidation potentials have been reported as the onset to oxidation rather than the peak potential or $E_{1/2}$ as the oxidation process can be quite broad and the peak may not be resolved (as shown in Figure 10C for **20**) because of large capacitive charging processes coupled with the faradaic response occurring over a large potential window. This can also be attributed to the presence of a range of conjugation lengths forming a wide distribution of redox centers.

In many cases, the technique of differential pulse voltammetry (DPV) is an indispensible, yet highly underutilized tool. This method utilizes small pulses that are superimposed on a linear voltage ramp with the current sampled before the pulse and at the end with the first current sample subtracted from the second. The voltammogram is then a plot of this current difference as a function of applied potential. With DPV, the faradaic current is measured after sufficient decay of the nonfaradaic charging current, potentially providing better resolving power of the onsets and peaks for oxidation and reduction over direct current measurements such as CV and chronoamperometry. DPV plots for both **2** and **20**, a polymer for which a clean oxidation onset is difficult to determine by CV, are shown in panels B and D in Figure 10. In addition to $E_{1/2}$ and oxidation onsets, electrochemical measurements can provide insight into redox reaction kinetics, reversibility of the redox process, and electron transfer rate constants. As one can gather, the information regarding electrochemical processes of films of conjugated electrochromic polymers is extensive and a comprehensive discussion is beyond the scope of this review. However, if the reader desires more information than the short overview provided here, we guide them to the references of Heinze,[64] Rajeshwar,[63] Audebert,[62] and Monk.[17]

Spectroscopy. Spectroscopic characterization of the optoelectronic properties remains as one of the most valuable methods in the characterization toolbox for electrochromic polymers. Most of the polymers discussed previously are cathodically coloring with their neutral state absorption present in the visible region, as is shown in Figure 11 for polymer **2**. This absorption arises from the onset of the $\pi-\pi^*$ electronic transition, also known as the interband transition, or bandgap (E_g). The spectra shown for this polymer has a broad absorption with a single maximum absorption peak (λ_{max}) observed. However, many systems show multiple absorptions for the neutral state. One such case is that of **4c**, which exhibits a splitting of the absorption into multiple peaks (shown in Figure 1) that can be attributed to vibronic coupling typically seen in systems that have highly ordered

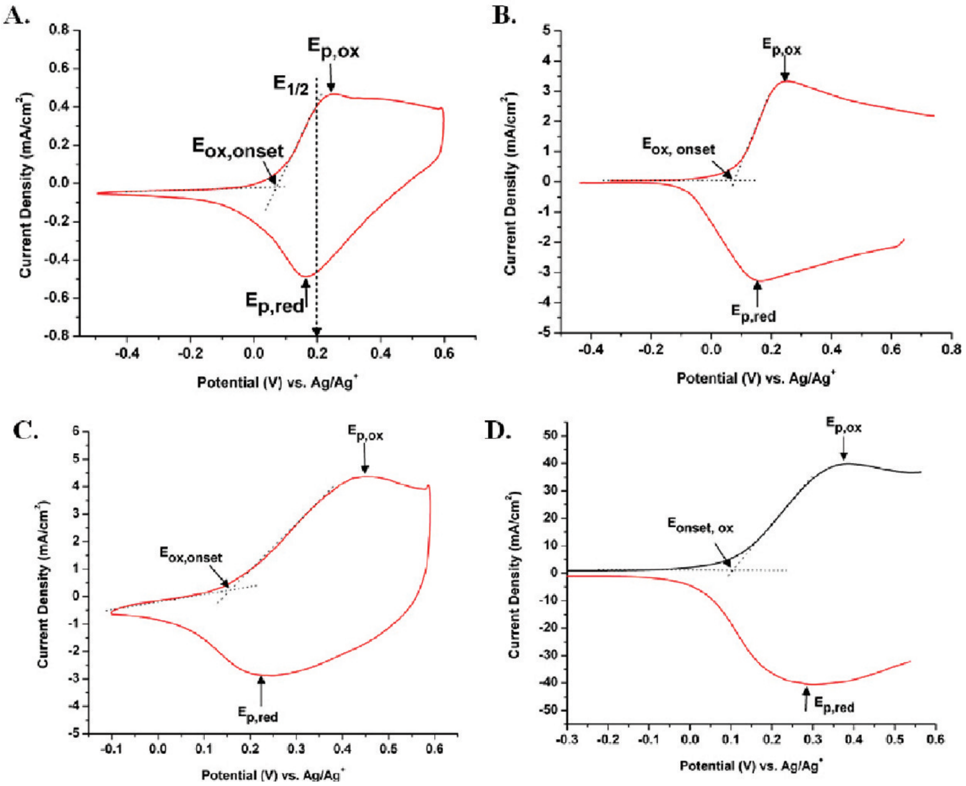


Figure 10. CV scans of drop-cast films of polymers (A) **2** and (C) **20** on Pt button electrodes. The peak oxidation potential is represented by $E_{\mathrm{p,ox}}$, peak reduction potential by $E_{\mathrm{p,red}}$, onset to oxidation by $E_{\mathrm{ox,onset}}$ and half-wave potential by $E_{1/2}$. DPV of polymers (B) **2** and (D) **20**. Data modified with permission from that originally presented in refs 34 (copyright 2010 American Chemical Society) and 55 (copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA).

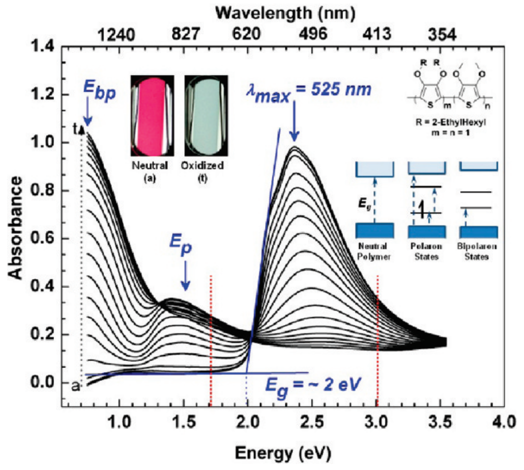


Figure 11. Spectroelectrochemical series for a film of **2** spray-cast onto ITO/glass in 0.2 M LiBTI/PC electrolyte switched from the neutral state (a) to the fully oxidized state (t). Inset shows photographs of the polymer film in the extreme states. Vertical red dotted lines denote limits of the visible region of the spectrum. Adapted with permission from ref 34. Copyright 2010 American Chemical Society.

structures in the solid state.[65] Further, the donor–acceptor systems exhibit two absorption peaks for the neutral state, as described previously, which can allow fine-tuning of the neutral state color with respect to the relative ratios of the two absorption peaks and the placement of the absorption minima (shown in Figure 1 for polymers **6a** and **12**).[20,27,28,30]

To further elucidate the optoelectronic properties of these thin polymer films, in situ spectroelectrochemical measurements are performed wherein the absorption (or transmittance) spectra are measured as increasingly higher oxidizing potentials are applied across the polymer film. As the polymer is oxidized, lower energy electronic transitions are introduced at the expense of the $\pi-\pi^*$ transitions, giving rise to electronic absorptions at longer wavelengths due to polaron and bipolaron (E_{p} and E_{bp}) carriers, whereas that in the visible begins to decrease as shown in Figure 11 and represented schematically in the inset. If these lower energy electronic transitions lie sufficiently outside the visible region (the limits of which are denoted by the vertical red dotted lines in the figure) with little tailing from the NIR, the polymer appears highly transmissive in the oxidized state. Although there are a number of polymers that oxidize to a near colorless, bleached state, in many cases, the loss of absorption in the visible region for the oxidized state is not complete and residual long wavelength absorption remains, giving the highly transmissive polymer a slight blue or gray hue. Although it is thought that a colorless bleached state is ideal, for many applications, a bleached state with a transmission of at least 80% across the visible window can be sufficient. For many reflective display applications, a faint blue or gray state can be overcome by color-matching the background reflector to the polymer bleached state color.

Colorimetry. A major weakness across research efforts in the field of electrochromic polymers is the lack of measurement of color and reporting of colorimetric

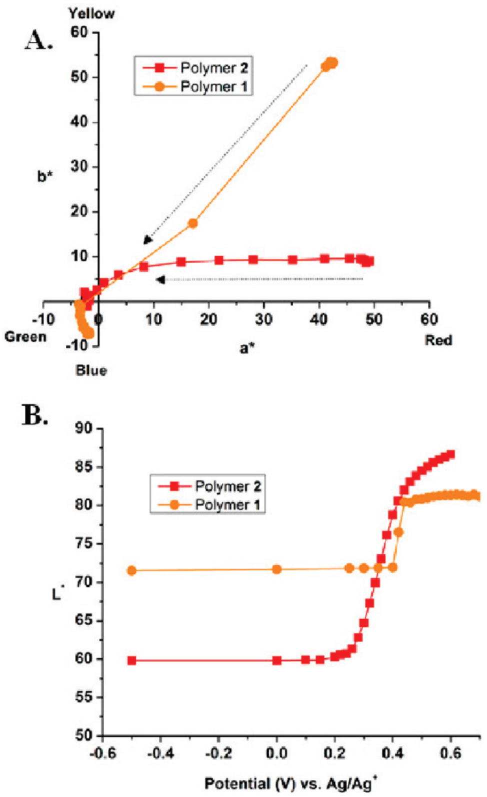


Figure 12. CIE LAB color coordinates for polymers **1** and **2** as measured using colorimetry during oxidation from the neutral states to transmissive oxidized states. (A) Plot of a^*b^* values and (B) L^* as a function of applied voltage. Each symbol indicates an applied potential and the arrows indicate increasing applied potentials.

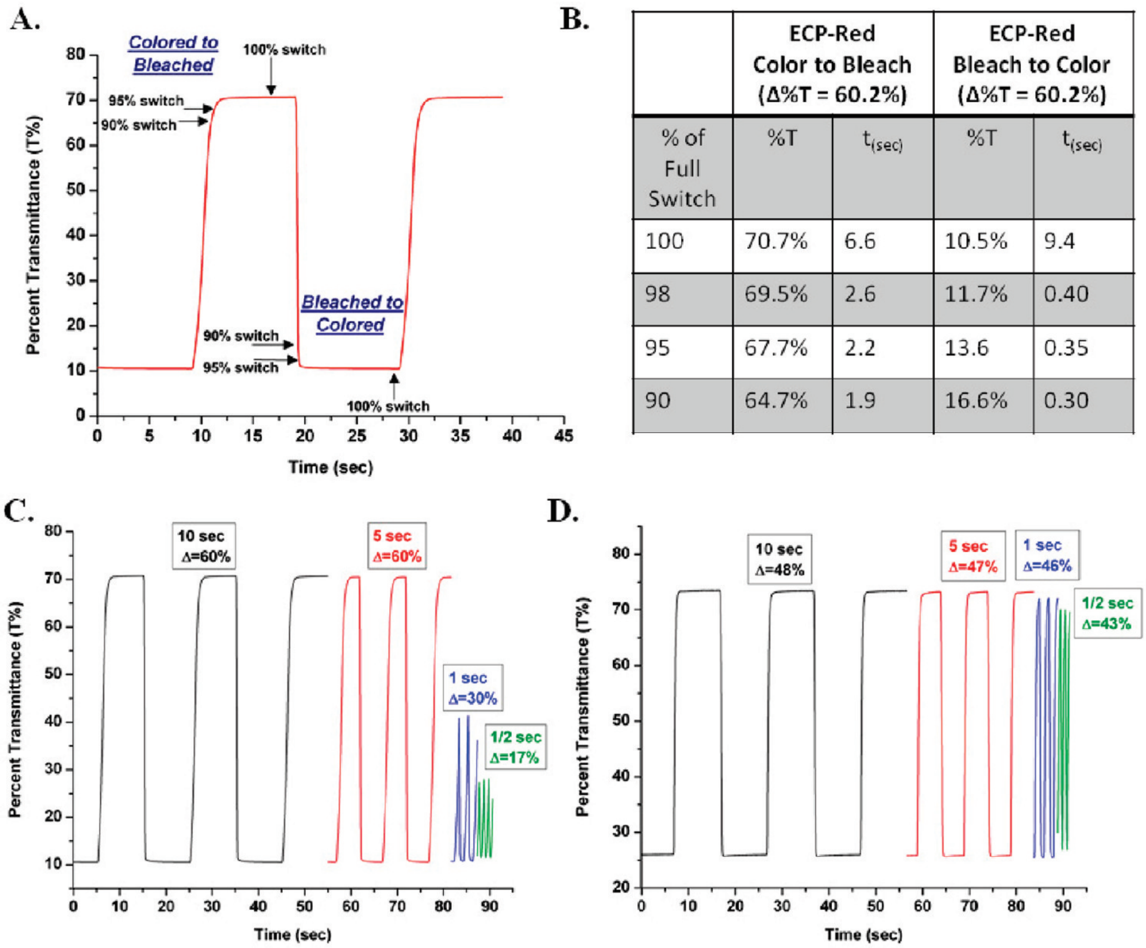
Table 1. CIE $L^*a^*b^*$ Values for Primaries As Given for the Reflective Munsell Colorchecker Color Rendition Chart

color	L^*	a^*	b^*
cyan	51.0	−28.6	−28.6
magenta	51.9	50.0	−14.6
yellow	81.7	4.0	79.8
red	42.1	53.4	28.2
blue	28.8	14.2	−50.3
green	55.3	−38.3	31.4
orange	62.7	36.1	57.1
black	20.5	−0.1	−1.0
white	96.5	−0.4	1.2

properties when covering the characterization methods of these materials. Colorimetry has been one of the most overlooked and misrepresented methods utilized. This is primarily due to the lack of consensus in how to apply this at times esoteric method to fundamental measurements of electrochromic materials. One of the most common methods to describe color with quantitative metrics is that devised by the Commission Internationale de l'Eclairage beginning in 1931.[66,67] Since that initial development of a color measurement system, there have been several iterations following, many of which have encompassed several books and manuscripts, and are certainly beyond the scope of this review.[66−71] To keep things simple, we will focus our attention on the system most readily adaptable to the measurement of the color of a thin film of an electrochromic polymer under standard lighting conditions; the CIE 1976 $L^*a^*b^*$ color space.

There are several sources detailing the theory of colorimetry and the history in the development of the standard colorimetric observers and derivations of tristimulus values that we will not cover here. However, the inquisitive reader is directed to the previously listed sources for an in-depth look at these subjects. We will state that colorimetry is a method used to numerically represent color of a sample through measurement of the sample spectra illuminated by a standard source and weighted such that the sensitivity of the human eye to light of different wavelengths is taken into account. There are several methods utilized to measure colorimetry with instrumentation available to digitally output values by a point-and-shoot method and others that are simply spectroradiometers or spectrophotometers with software available to output colorimetric values. Although a number of instruments provide a calibrated light source that can be software corrected to represent the standard illuminants suggested by the CIE (i.e., standard illuminant A, D50, and D65),[66] others do not and standard lighting systems, or viewing booths, need to be utilized. This is an often disregarded factor, and yet important for accurately representing color as the CIE system is based on viewing the sample measured under lighting conditions that closely resemble those that the subject would most commonly be viewed such as tungsten filament lighting (i.e., illuminant A), and natural daylight (e.g., D50-horizon light, and D65-noon light). A commonly utilized measurement method reported is that of transmission mode with the measurement of the polymer film on a transparent electrode (e.g., ITO/glass) while illuminated from behind with a standard light source (e.g., D50 or tungsten halogen corrected for D50).[71]

Whereas the original defined color space is that of CIE 1931 Yxy, the most applicable to electrochromic applications is that defined in 1976 and is the CIE $L^*a^*b^*$ or CIELAB color space with the CIE Yxy and CIE $L^*u^*v^*$ most applicable to emissive display applications. A typical representation of the a^*b^* color track of an electrochromic polymer film during oxidation is shown in Figure 12A and the variation of L^* (or lightness) with applied potential during oxidation in Figure 12B. The CIELAB color space is a color-opponent space that approximates color as the human brain perceives it. Here, L^* represents the lightness of the color from 0 to 100 (black vs white), a^* represents how much red versus green (green for $-a^*$ values and red for $+a^*$ values), and b^* represents how much yellow versus blue (yellow for $+b^*$ values and blue for $-b^*$ values) a color contains. As can be seen for polymer **1**, the neutral state has a^*b^* values that place it central between yellow and red, which is expected as this polymer has a neutral orange state. As the polymer is oxidized, the a^*b^* values decrease, indicating a loss of color, with the fully oxidized state having a highly transmissive faint blue tint. Similarly with polymer **2**, the neutral state a^*b^* values indicate a saturated red color with the oxidized film having a near colorless state. The third dimension of color, luminance or L^*, is shown in Figure 12B for polymers **1** and **2**. As both polymers are oxidized, the L^* value increases indicating an increase in the perceived "lightness" of the film.



	ECP-Red Color to Bleach (Δ%T = 60.2%)		ECP-Red Bleach to Color (Δ%T = 60.2%)	
% of Full Switch	%T	$t_{(sec)}$	%T	$t_{(sec)}$
100	70.7%	6.6	10.5%	9.4
98	69.5%	2.6	11.7%	0.40
95	67.7%	2.2	13.6	0.35
90	64.7%	1.9	16.6%	0.30

Figure 13. Response time for (A) polymer **2** when switched from fully neutralized and fully oxidized with 10 s hold at each potential. (B) Percent transmittance and time to reach that value at various stages of the full optical contrast for (C) polymer **2** and (D) polymer **12**.

To allow the reader perspective on the primary colors sought, Table 1 contains the $L^*a^*b^*$ color coordinates for the various primaries as given by the Munsell Color-Checker color rendention chart used in photography, paint, and printing industries. Given that there is no “ideal” standards specified for the various display industries and the colors used vary widely depending on use and manufacturer, the values given are only meant to give perspective and are not meant to represent standards.

Response Time. For many applications, such as electrochromic windows, the time desired to reach a full optical switch can be on the order of several minutes. Yet, for others such as active or video displays, the time required decreases to tens of milliseconds. When discussing the rate at which an electrochromic polymer film switches, there are two considerations: the time necessary for the full (or a specific percent of full) optical contrast to be reached and the contrast reached when the film is switched at a specific rate. As shown in Figure 13A and B for polymer **2**, when the film on ITO/glass is switched between fully neutralized and fully oxidized, the time to reach full optical contrast is 6.6 s when switched from colored to bleached and 9.4 s when switched from bleached to colored. This asymmetry is not unexpected as various factors, such as differences in conductivity of the electrochromic polymer, electric field strength, film solvation, and the dominant mobile ion diffusion rates within the film, occur based on the switching direction. However, it is known that the human eye is fairly insensitive to single digit changes in transmittance, and for many display oriented characterizations, the time to reach anywhere from 90 to 95 or 98% of the full optical contrast is reported. These times can be considerably less than the full (100%) optical switch as the largest fraction of the redox process occurs within the first portion of the voltage pulse. As the potential across the film is held constant and the current decays, a small portion of sites are still undergoing the redox process. This is due to the fact that the rate at which the redox switch occurs is limited by the diffusion and migration of charge balancing counterions within the polymer film as the electronic and ionic effects are strongly coupled. This can be seen in the table in Figure 13B where the time to reach the bleached state at 100% of the full switch of 70.7% is 6.6 s whereas the time to reach 90% of that switch (64.7%) is only 1.9 s. That time is much less for the switch from the fully bleached to fully colored state with 90% of the full switch reached in 300 ms.

This coupling of the electronic and ionic effects also influences the contrast achieved when switching the polymer film at faster switch rates repeatedly. Panels C and D in Figure 13 compare the optical contrast maintained when decreasing the switching time from 10 to 5 s, 1 s, and finally half a second for polymers **2** and **12**. As can be seen, polymer **12** maintains a relatively high (43%) contrast with only a 5% decrease when the time the polymer film is held at each potential is decreased from 10 to 0.5 s. On the other hand, polymer **2** exhibits a drop from 60% contrast to 17% contrast. This is possibly due to the less compact nature of the cast film of **12** relative to **2**, allowing for faster and more facile ion−solvent ingress and egress from the film when repeatedly switched between the voltage extremes. It should be noted that these comparative observations are not a global phenomenon across all electrochromic polymers but specific to these two examples given.

Composite Coloration Efficiency. In considering the practical applications of electrochromic materials in display and window devices, the amount of energy to affect a color change is an important consideration. Many researchers report values of coloration efficiency that considers these values; however, a full account of the color change produced *during* a switch is rarely considered. This can be estimated through the calculation of composite coloration efficiency (CCE, η).[72,73] CCE is calculated as the ratio of the change in optical density to the charge density passed during the switch, $\eta = \Delta OD/\Delta Q_d$. CCE is measured by utilizing a simultaneous chronocoulometry (with a square wave potential profile applied) and chronoabsorptometry experiment, with the percent transmittance during the switch monitored at the absorbance maxima. It should be noted that the potentials applied should be between the voltage extremes to cause the full optical switch and can be stated for any degree of the full switch (clearly indicated) such as 95 or 98% of the full optical switch as previously described for measurements of response time. The previous publication by Gaupp et al.,[72] thoroughly details the measurement of composite coloration efficiency and, as such, we direct the interested reader there rather than reproduce that information here.

Cycle Life. A final important factor in evaluating electrochromic materials is the determination of cycle life. This practical measurement (controlled by a number of parameters) provides information on how many full switch cycles can be performed for an electrochromic film before measurable degradation occurs and is an indicating factor of the electrochrome durability. There is little consistency in how these measurements are conducted with many authors utilizing cyclic voltammetric cycling and others utilizing square wave voltammetry to cycle between the voltage extremes in addition to many authors reporting the lifetime to a number of cycles while others report the lifetime to a specific time after switching began. Further, many authors report only the current density with respect to time to represent the amount of degradation through current loss and others measure the amount of optical contrast lost. Understandably, the cycle life of a material can depend strongly on the electrolyte utilized, the potential range (full or partial switch), switch speed, and exposure to (or lack thereof) oxygen or light, and as such, all factors should be stated when reporting cycle life. While there is little consensus among the field on the previously detailed characterization methods, cycle life is one of the methods with the least amount of consistency. As such, the reader is cautioned to scrutinize the conditions under which cycle life values are reported and understand the difficulty in applying direct comparison between materials.

Processing and Patterning of ECPs

Much of the past, and current, efforts in the area of patterning and film formation of electrochromic polymers and devices has involved primarily electropolymerizable systems. However, there has been extensive progress in the field of printing, patterning, and processing of soluble conjugated polymers for electronic and optoelectronic applications such as light-emitting displays, field effect transistors, and even photovoltaics.[74−80] Although there are several examples of the demonstration of printing conjugated polymers for electrochromics, which we will cover in detail here, one could imagine that many of the printing methods utilized for various other applications could be extended easily to soluble polymer electrochromes. Given the vast number and variety of printing and processing methods available to soluble polymers, we do not intend to cover all possibilities; rather, we will cover the most common and those that hold the most promise to extend to large-scale printing and fine patterning for electrochromics. While there have been examples of the use of drop-casting or spin-coating for the processing of polymer films, and although these two methods have been repeatedly utilized in the processing of films for polymer light-emitting devices or photovoltaics, their practicality in processing of electrochromics is limited at best. First, the highly ordered, compact films required for these aforementioned solid state devices is a detriment in electrochemical devices such as electrochromics where a porous, open morphology is desired for facile ion diffusion. Second, while high visual quality films can be achieved for rather thin films (~100 nm) from spin-coating, high-quality films at the thicknesses required (0.3−1 μm) for high contrast EC applications are rather difficult to obtain. Third, both methods are limited in the ability to actively control film thickness with drop-casting limited to thick films and spin-coating limited to thin films. These factors listed, in addition to the limited practicality in utilizing these methods for large-scale printing/processing, have led the authors to the opinion that the methods following, not spin-coating or drop-casting, will become dominant in the furthering of processing soluble electrochromic polymers and as such will be exclusively covered. Additionally, there are a variety of examples of printing and patterning electrode materials, specifically for use in electrochromic device applications.[81−85] Although these patterned electrodes lead to a large number of possibilities for finite and intricate detailed patterns, it is beyond the scope of this review.

Spray-Casting. One of the most widely used, and straightforward methods for processing soluble conjugated polymers is that of spray-casting (also referred to as gas atomized spraying).[27,30,34,41,86] This method utilizes a simple pressurized airbrush sprayer (typically available in commercial art supply stores and hobby shops) to cast the polymer on an electrode surface from a solution of the polymer

Figure 14. Pattern obtained by spray-casting through a shadow-mask of a variety of available EC polymers as discussed in the previous sections. Reproduced with permission from ref 34. Copyright 2010 American Chemical Society.

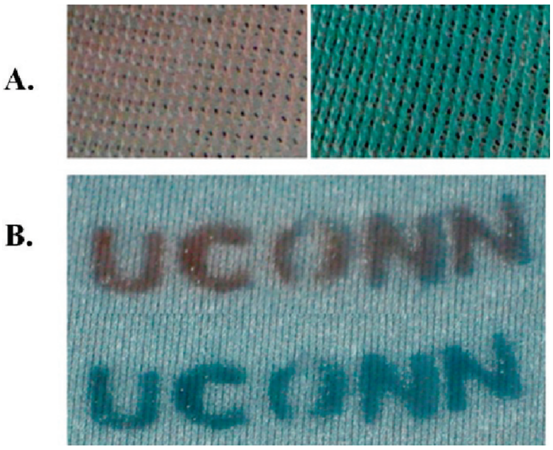


Figure 15. Demonstration of electrochromism on fabric electrodes with a soluble EC polymer spray-cast onto a Spandex fabric electrode. (A) EC polymer-coated Spandex in electrolyte bath, stretched, switching between neutral (left) and oxidized (right) states. (B) Patterned EC polymer on fabric electrode in neutral (top) and oxidized (bottom) states. Adapted with permission from ref 87. Copyright 2010 American Chemical Society.

dissolved in a solubilizing solvent. These solvents can be typically toluene or chloroform (or other volatile organic solvents for organic soluble polymers), or water or methanol (for aqueous and alcohol soluble polymers). Although the resulting polymer film can appear rather homogeneous to the eye, the typical spray-cast film topography is relatively rough with an average roughness on the order of several tens to hundreds of nanometers.[86] However, for a simple, low-cost, and quick processing method to obtain film thicknesses in the range of 50 nm to several micrometers, spray-casting is the most straightforward approach. In Figure 14, we show an example of the variety of patterns that can be obtained by spray-casting through shadow masks. Each of the examples is of multiple colored polymers spray-cast onto a continuous ITO electrode.

An additional advantage of spray-casting for a processing method is that the polymer films can be cast onto a variety of substrates (conducting or insulating) of varying sizes and shapes with films having been demonstrated to be spray-cast on steel mesh and Spandex fabric-based electrodes as shown in Figure 15.[87]

Screen- and Flexoprinting. Another widely applicable method for electrochromic film processing is that of screen-printing. This method has been widely utilized for fabrication of printed and patterned layers for solar cells and light-emitting diodes with the active layer and electrode materials printed.[75,79,80,85,88] There have been several reports of screen printing active electrochromic layers with materials such as PEDOT:PSS processed from aqueous dispersions the most common.[89−91] Similar printing methods, such as rotogravure and doctor blade printing are also viable options with the most well-demonstrated method of flexographic printing used to print PEDOT:PSS electrodes in a roll-to-roll method, further demonstrating the commercial attraction to large-scale printing of soluble polymers.[76] An example is shown in Figure 16 for flexoprinting as used by Acreo in Norrköping, Sweden to print all-organic displays on either paper or plastic substrates.

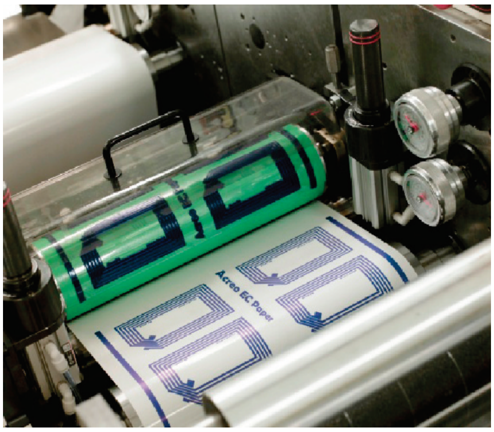


Figure 16. Use of flexoprinting to print PEDOT:PSS layers on flexible substrates at Acreo. Reprinted with permission from Acreo AB.[76]

Inkjet Printing. Another common conventional printing/patterning method is that of inkjet printing. As with the screen printing method, there are a large number of examples of the use of inkjet printing to prepare active layers for polymer photovoltaics, light-emitting displays, and polymeric electronic devices,[74,77,78,92] but very few on patterning of polymeric electrochromics. The few examples that do exist involve the printing of aqueous solutions of polyaniline and PEDOT as composites with carbon nanotubes or silica colloids.[93,94] Inkjet printing is a rather advantageous method for patterning electrochromic polymers as it can be accomplished with modified domestic printers, as demonstrated in the two examples listed in Figure 17, or with commercial inkjet printing systems for large-scale printing, printing on rigid substrates, or nonaqueous solvent printing. As shown in the inset to Figure 17, patterns can be printed with feature sizes on the order of several millimeters.

Photolithography and Soft Lithography. While not yet extensively demonstrated in the literature for electrochromic polymers, the method of photolithography is one that could conceptually be applicable. The methodologies demonstrated for conjugated electroactive polymers have included the use of chemically amplified photolithography, electron beam lithography, and photo-cross-linking of precursor polymers to obtain patterning for LEDs, diffraction gratings, and actuators.[95−101] A use of photolithography for patterning of oligomeric electrochromes was discussed previously and shown in Figure 7 for a material that can be patterned through cross-linking of

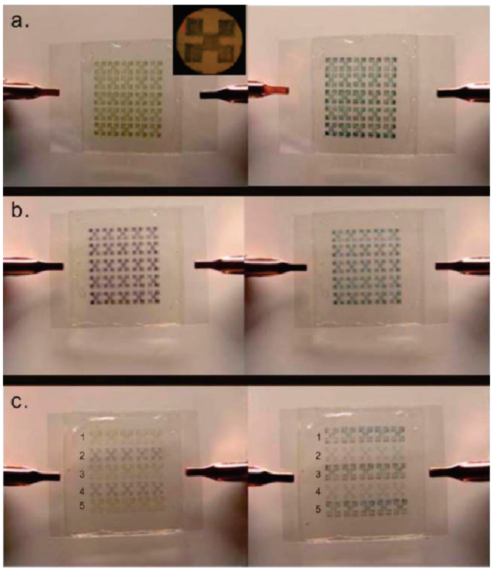


Figure 17. Demonstration of inkjet printing of solution processed EC polymers in devices. (a) PANI-based film, (b) PEDOT-based film, (c) dual PEDOT and PANI-based film with rows 1, 3, and 5 PANI and rows 2 and 4 PEDOT. The photographs are of the devices at −2 V (left) and +2 V (right) with the 5 × 5 arrays containing 5 square pattered pixels that are each 500 μm × 500 μm. Reproduced with permission from ref 93. Copyright 2008 The Royal Society of Chemistry.

the yellow-to-blue-to-gray switching material.[53] Another demonstration of the use of photolithography for patterning an electrochromic polymer was that of using chemically amplified photolithography to pattern films of a modified EDOT polymer.[95]

In this demonstration, the THP-functionalized EDOT was cast in the presence of a photoacid generator and the resulting film exposed to radiation through a shadow mask that initiates the acid catalyzed deprotection of the functionalized EDOT, rendering the exposed areas insoluble. The unexposed regions were then rinsed away, leaving a negative pattern of the photomask.

A similar example of utilizing photolithography to pattern a conjugated polymer used direct thermal patterning of a conjugated polymer modified with a thermally labile functional group.[96] The polymer was blended with a NIR sensitive dye that, upon localized heating, catalytically eliminated and volatilized the functional group, once again, rendering the patterned areas insoluble. Feature areas with micrometer size resolution were reported.

Soft lithographic methods utilized to pattern electroactive polymers include micromolding in capillaries (MIMIC) which was used to produce feature sizes in the range from 350 nm to 50 μm of PANI and a thiophene-benzothidiazole-based oligomer.[102,103] Alternatively, the method of nanoimprint lithography has been demonstrated for films of blends of PANI or PEDOT with plasticizers, and polyterthiophene-based precursor polymers.[104−106] One of the few demonstrations of soft lithography to pattern electrochromic films was by Admassie and Inganas wherein they patterned PEDOT:PSS films by pressing a patterned stamp into a previously spin-cast polymer film on ITO/glass.[97] The wet PEDOT:PSS film was imprinted with the pattern of the stamp (that of a diffraction grating) and allowed to dry, yielding features with 1.5 to 3 μm spacings. The polymer films switched between the typical light blue and dark blue of PEDOT with the films exhibiting diffraction of incident light.

Among the various other methods available to process and print soluble conjugated polymers, electrostatic methods can be considered some of the more exotic with techniques such as electrospinning, electrophoretic patterning, and even electrostatically driven dip-pen nanolithography (DPN) among them.[107−109] All three methods listed require a highly charged surface on which to print the polymer. In the cases of DPN and electrophoretic patterning, the polymers themselves must also be charged, with the examples given including doped polymer solutions such as polypyrrole and PANI.[107,108] Direct patterning of fine structures (on the order of hundreds of nanometers) have been achieved with these polymers. While not yet demonstrated, it can be envisioned that these methods can be applicable to the various polymers described earlier by oxidation of the polymer solutions prior to printing.

As stated earlier, although there are many examples of printing and processing of soluble conjugated polymers using a variety of methods (many low-cost high yield, and others applicable to fine structure patterning) there has not been a strong push to utilize these methods in processing electrochromic polymers. The possibility now exists for these methods to be explored as the availability of highly soluble multicolored electrochromic polymers is increasing.

Electrochromic Devices (ECDs)

While the synthesis and fundamental characterization of electrochromic polymers is essential in furthering the field with respect to understanding structure−property relationships and how the color palette can be extended to create materials to stimulate commercial interest, it is the incorporation of these materials in device structures and subsequent testing (albeit on a laboratory level) that will demonstrate practical usage. Many of the devices disclosed in the literature, however, are those comprising inorganic (metal oxide or transition metal complex), and small molecule organic (viologens) materials as the active layers or as counter electrode materials to conjugated polymers. The possible reason for a smaller proportion of devices discussed utilizing conjugated polymers as active and counter materials is the limited availability of commercial electrochromic polymers. Many of the primarily synthesis and characterization-based research groups that synthesize new materials do not wade into the deep waters of device construction and engineering. At the same time, many of the groups engineering devices do not have access to the new solution processable materials besides PEDOT and PANI, explaining the large amount of literature disclosing devices constructed utilizing these two materials. If the field is to push further ahead and see commercial applications of the multicolor polymers, a strong collaboration between the materials “creators” and device “builders” needs to be cultivated.

Here, we will cover the electrochromic devices presented in the scientific literature (disregarding the patent literature) constituting electrochromic polymers as active coloring and charge balancing materials with discussion on common device types (transmissive, reflective, and lateral) and electrode materials. As mentioned previously, many of the devices represented in the literature contain PEDOT and/or PANI as the active materials. As such, we will be showing those here with the expectation that the soluble materials discussed previously in this review could easily be incorporated into similar device architectures, if they have not already.

Absorptive/Transmissive Devices. The most commonly utilized device architecture is that of the absorptive/transmissive type of device and understandably so as electrochromic windows are of intense interest in the commercial and academic fields for privacy and energy savings applications. The typical construction is that as shown in Figure 18 with the device comprised of two transmissive electrodes arranged facing each other and coated with electroactive materials, electrochromic polymers in this case, and an electrolyte layer in between.

The electrodes selected are transmissive to the wavelengths of interest, typically the visible region of the spectrum but wavelengths outside the visible (i.e., the near-infrared) are increasingly becoming of interest.[110−114] For high visible region transmissivity, indium doped tin oxide (ITO) is the most common choice with the substrate comprised of either glass, for rigid devices, or plastic, for flexible devices. However, the flexibility of ITO on plastic is fairly limited with the conductor cracking and a loss of conductivity occurring limiting the bending radius of ITO-based flexible electrodes. Several alternative conductors deposited on plastic for flexible electrodes have been developed with examples being graphene,[115] single-walled carbon nanotubes,[82,112,116] and PEDOT:PSS.[81,117] The graphene and SWNT-based electrodes also offer the advantage of superior transmissivity in the NIR and IR regions of the spectrum for long-wavelength light modulation.

In an effort to decrease the number of layers in absorptive/transmissive devices, Chevrot et al., have developed free-standing films of a semi-interpenetrating network of PEDOT polymerized in a cross-linked poly(ethylene oxide) matrix containing an electrolyte (a salt dissolved in propylene carbonate or an ionic liquid). These self-supported films contain a higher loading of PEDOT on the outer edges and a depleted region in the center. When the film is sandwiched between two transparent electrodes, a transmittance contrast of 33% is achieved in the visible region.[118,119]

In most applications, the device is desired to switch reversibly from a highly absorptive state to a highly transmissive state. As the device operates with a voltage applied to one of the electrodes and a voltage of opposite polarity is applied to the other, the electrochromic polymers at each electrode should be optically complementary when in these opposite charged states. An electroactive species at each electrode is necessary to aid in balancing the charge passed at each electrode. Without a counter polymer layer, devices typically switch at higher voltages, with lower optical contrast and are less stable.[120] Although it is commonly reported to use the same electrochromic material at both electrodes, for example, PEDOT or PANI at both the working and counter electrode, these devices typically exhibit a lower optical contrast, as both materials cannot simultaneously be in their most absorptive and most transmissive states when the device bias is switched.

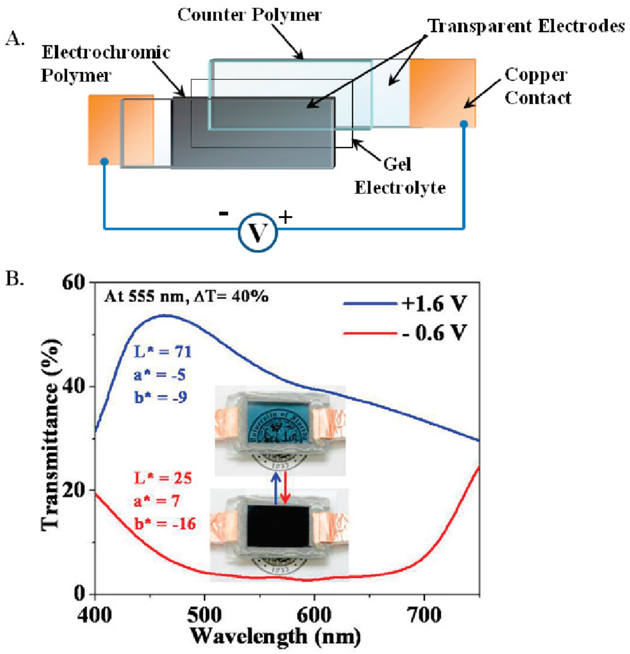


Figure 18. (A) Schematic of a typical absorptive/transmissive electrochromic "window", and (B) an example of a black to transmissive device as reported by Shi et al. Reproduced with permission from ref 55. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

To improve the contrast in window-type devices, researchers have utilized a cathodically coloring polymer at one electrode and an anodically coloring polymer at the other. An early, and often repeated, example is that of dimethyl-ProDOT and BisEDOT-*N*-methyl carbazole both electrochemically polymerized at an ITO/glass electrode.[121−123] When the device is assembled, one polymer, the poly(dimethyl-ProDOT), is in the fully neutralized and highly absorptive state while the poly(bisEDOT-*N*-methyl carbazole) is in the fully oxidized, colored, state. This device exhibits a 56% Δ*T* contrast, switching from an absorptive blue-purple to a highly transmissive light green as the poly(dimethyl-ProDOT) switches from a purple neutral state to highly transmissive light blue and the poly(bisEDOT-*N*-methyl carbazole) switches from a blue oxidized state to transmissive yellow neutral state.

To improve the optical contrast, Reynolds et al. developed a series of anodically coloring, high-bandgap *N*-substituted ProDOPs, such as PProDOP-*N*-PrS that is highly transmissive, near colorless in the neutral state, and light gray-green in the oxidized state.[121] However, as reported by Padilla et al.,[124] the optical contrast of a dual polymer device is limited and will always be lower than the contrast of the individual electrochromic materials except in

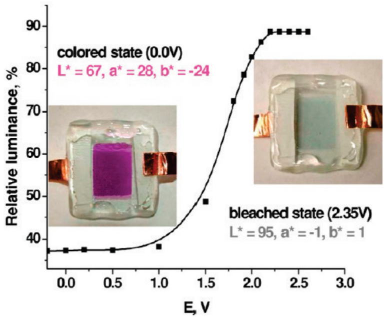


Figure 19. High contrast, vibrantly colored absorptive/transmissive ECD utilizing a noncoloring electroactive material at the counter electrode. Reproduced with permission from ref 116. Copyright 2009 American Chemical Society.

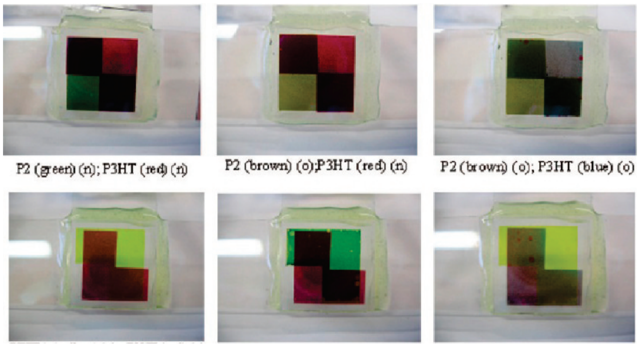


Figure 20. Example of multiple colors accessible in a layered-type device as reported by Beaupré et al. for spray-processed films of P3HT and a carbazole derivative. Reproduced with permission from ref 126. Copyright 2009 American Chemical Society.

the case where a material is used at the counter electrode that is electroactive and either is not electrochromic, or has little color change during switching. One such material that fits this description is the propionitrile-substituted PProDOP that is an electrodeposited film and is highly transmissive in both neutral and oxidized states, yet highly electroactive, providing sufficient charge balance during device switching.[54] This is possible as the polymer is a high bandgap material with a neutral state absorbance in the UV. Upon oxidation, the absorption shifts into the NIR, with little optical density in the visible region. A related material is the organic soluble *N*-alkyl substituted PProDOP that exhibits very little coloring during switching and has been demonstrated to be an efficient charge balancing material in a black to transmissive switching electrochromic device as shown previously in Figure 18.[55]

Further steps toward developing efficient counter electrode materials for electrochromic devices was advanced by Nishide et al., with their use of a radical polymer containing a redox-active tetramethylpiperidin-N-oxyl (TEMPO) group.[125] This material is highly electroactive with no color change in either redox state, allowing for the device to switch with an improved contrast and color purity over that which would have been achieved with previously available counter electrode materials. Following Nishide's work, Vasilyeva et al., have reported further demonstration of the improved contrast of a device, as shown in Figure 19, using the solution processable **4c** (as described previously) as the active electrochrome and a TEMPO-based polymer, PTMA, blended with PMMA acted as the charge balancing counter material.[116] An absorptive/transmissive type of device was constructed utilizing both materials on ITO/glass, showing a transmittance contrast of ~70% with a high transmissivity in the bleached state of 95%.

In addition to reaching higher optical contrasts and maintaining color purity in window-type devices, researchers have focused on extending the color palette in a single device as shown in the photograph in Figure 20 by Leclerc et al.[126] These devices utilize spray-processed carbazole-based polymers and P3HT to create multicolored devices that switch from shades of green, red, blue, yellow, and brown for adaptive camouflage-type applications. Further, Reynolds et al. have reported a layered device structure using two active polymer layers and two counter polymer layers on separate four ITO/glass electrodes.[54] Using bipotentiostatic control, each of the two active polymer layers could be independently controlled to yield a full palette of colors that include green, purple, black, and a highly transmissive state at the extremes.

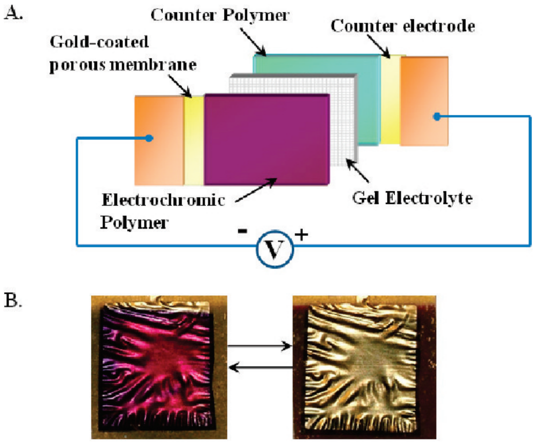


Figure 21. (A) Schematic of an absorptive/reflective ECD and (B) photographs of a device in the colored (left) and reflective (right) states.

Absorptive/Reflective Devices. Another type of device structure commonly utilized for processable electrochromic polymers is the absorptive/reflective device. Of this device type, there are two structures most often reported: those based on specular reflectance (as shown in the schematic in Figure 21) and those based on diffuse reflectance. The specular reflective-type of devices operate with one of the electrodes as the reflector. As shown in Figure 21A, the working and counter electrodes are arranged such that the working electrode is forward-facing and the counter electrode is hidden behind. The working electrode should be porous, either a metalized porous membrane or a slitted electrode to allow for ion diffusion during switching of the device.[40,110,111,114,127−129] Relatively high reflectance contrasts have been obtained with this type of device as the counter electrode is hidden and the optical properties of the counter material do not affect the device contrast, only providing charge balancing. As such, a larger variety of materials can be

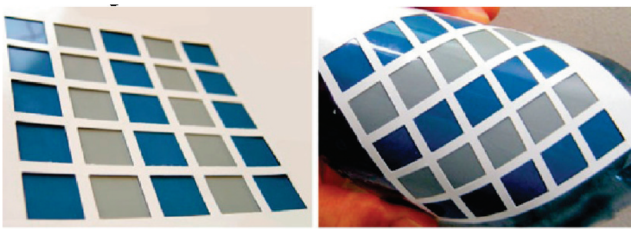


Figure 22. Demonstration of all printed PEDOT-based electrochromic devices that are fully flexible. Reproduced with permission from ref 91. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

utilized at the counter electrode, such as the same material at the working electrode, with the only two requirements being a sufficient charge density during switching and electrochemical stability within the switching voltage of the device. Another advantage of this device type is that the most often used electrode material is a gold-coated porous membrane. Given that gold has a large IR reflectivity, these devices are advantageous platforms for characterizing the IR electrochromic switching properties and utilization for space,[111,127] thermal, and optical telecommunications applications.[110] For example, Chandrasekhar has demonstrated effective use of these devices for thermal signal camouflage[127] and Dyer et al., have demonstrated that the large NIR reflectivity has the possibility to be utilized in optical telecommunications as a variable optical attenuator.[110]

The diffuse reflective device is constructed similarly to the window-type device with the working and counter electrodes arranged such that they face each other. The reflection occurs off a reflective material dispersed between the two electrodes. The counter electrode is still hidden with the color properties not contributing to the device colors and contrast, as was the case with the specular reflective devices. The reflective material is typically TiO_2 particles dispersed in the electrolyte giving the device a colored to reflective white appearance as shown in Figure 22.[89,91] These devices are display-type with the white reflective state high enough that the devices can act as paper mimics. The devices disclosed by Berggren et al. typically contain PEDOT:PSS as the active switching electrochrome, but they have also evaluated several active materials with the intention of increasing the contrast over that of the PEDOT alone.[89,130] In addition to being fabricated from solution processable materials, allowing printing of the devices, they are fully flexible, as can be seen in the photographs. This demonstrates all-organic displays with various additional possibilities through the use of active matrix pixels allowing independent addressing.

Lateral Devices. A less commonly utilized, but potentially functional, device type is that of the lateral device. These devices operate with both working and counter electrodes on the same substrate and within the same plane.[81,131] This type of layout minimizes the number of layers, providing for a simplified device manufacture. However, as the current between the working and counter electrodes has to travel laterally across the electrode surface rather than orthogonal to it (as is the case in the previously discussed device types), the rate and contrast at which the devices can switch are lowered. As the line patterns and line spacing becomes smaller, the contrast and switch speed increase, but complexity in device design and construction increase with lithographic electrode patterning being necessary in many cases.

Perspective on the Field

If one considers the development of this field, it is evident that the early work on electropolymerized films established the basis for structure−property relationships that now allow a high degree of color control in the ECPs. Taking a lesson from others who have developed soluble π-conjugated polymers for semiconducting applications, the utilization of pendant groups of varied conformational flexibility, polarity, and ionicity have yielded ECPs that can be processed to large area switchable films and patterned by a myriad of methods. Certainly, the chemistry is not yet done as considerations of further color tuning, polymer:ion interactions, electrode adhesion, and other important consideration will continue to be developed. Analytical methods will play an important role in determining the utility of materials to certain applications, in developing a deeper understanding of the electrochromic effect, and in providing useful comparisons of materials. With that said, the field of polymer electrochromics are on the verge of practical utility and are ready to be tested and utilized in a number of window- and display-type architectures which might include flexible appliqués, smart cards, point-of-purchase advertising, along with many others.

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References

(1) *Conjugated Polymers: Processing and Applications* (*Handbook of Conducting Polymers*), 3rd ed.; CRC Press: Boca Raton, FL, 2007.
(2) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.
(3) McCullough, R. D. In *Conjugated Polymers: Processing and Applications* (*Handbook of Conducting Polymers*); Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2007.
(4) Groenendaal, L.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 855.
(5) Kirchmeyer, S.; Renter, K.; Simpson, J. C. In *Handbook of Conducting Polymers*; 3rd ed.; Skothheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2007.
(6) Grimsdale, A. C.; Leok Chan, K.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.
(7) Tsao, H. N.; Cho, D.; Andreasen, J. W.; Rouhanipour, A.; Breiby, D. W.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 209.
(8) Katz, H. E.; Huang, J. *Annu. Rev. Mater. Res.* **2009**, *39*, 71.
(9) Gong, X.; Tong, M.; Xia, Y.; Cai, W.; Moon, J. S.; Cao, Y.; Yu, G.; Shieh, C.-L.; Nilsson, B.; Heeger, A. J. *Science* **2009**, *325*, 1665.
(10) Gilles, D.; Markus, C. S.; Christoph, J. B. *Adv. Mater.* **2009**, *21*, 1323.
(11) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.
(12) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.

(13) Fan, L. Z.; Hu, Y. S.; Maier, J.; Adelhelm, P.; Smarsly, B.; Antonietti, M. *Adv. Funct. Mater.* **2007**, *17*, 3083.
(14) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.
(15) Chemburu, S.; Ji, E.; Casana, Y.; Wu, Y.; Buranda, T.; Schanze, K. S.; Lopez, G. P.; Whitten, D. G. *J. Phys. Chem. B* **2008**, *112*, 14492.
(16) Smela, E. *Adv. Mater.* **2003**, *15*, 481.
(17) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*; Cambridge University Press: New York, 2007.
(18) Dyer, A.; Reynolds, J. R. In *Handbook of Conducting Polymers*; 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2001, p 20.1.
(19) Argun, A. A.; Aubert, P.-H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chem. Mater.* **2004**, *16*, 4401.
(20) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.
(21) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41*−*43*, 831.
(22) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. *Adv. Funct. Mater.* **2002**, *12*, 89.
(23) Gustafsson, J. C.; Liedberg, B.; Inganäs, O. *Solid State Ionics* **1994**, *69*, 145.
(24) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347.
(25) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498.
(26) Durmus, A.; Gunbas, G. E.; Toppare, L. *Chem. Mater.* **2007**, *19*, 6247.
(27) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Adv. Mater.* **2008**, *20*, 2772.
(28) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nat. Mater.* **2008**, *7*, 795.
(29) Reeves, B. D.; Unur, E.; Ananthakrishnan, N.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 5344.
(30) Amb, C. M.; Beaujuge, P. M.; Reynolds, J. R. *Adv. Mater.* **2010**, *22*, 724.
(31) Icli, M.; Pamuk, M.; Algi, F.; OÌnal, A. M.; Cihaner, A. *Chem. Mater.* **2010**, *22*, 4034.
(32) Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Jost, R. W.; Rubin, Y.; Wudl, F. *Macromolecules* **2005**, *38*, 669.
(33) Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Funct. Mater.* **2008**, *18*, 2026.
(34) Dyer, A. L.; Craig, M. R.; Babiarz, J. E.; Kiyak, K.; Reynolds, J. R. *Macromolecules* **2010**, *43*, 4460.
(35) Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, *29*, 7629.
(36) Sankaran, B.; Reynolds, J. R. *Am. Chem. Soc. Proc., Div. Polym. Mater. Sci. Eng.* **1995**, *72*, 319.
(37) Havinga, E. E.; Mutsaers, C. M. J.; Jenneskens, L. W. *Chem. Mater.* **1996**, *8*, 769.
(38) Welsh, D. M.; Kloeppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, *35*, 6517.
(39) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250.
(40) Cirpan, A.; Argun, A. A.; Grenier, C. R. G.; Reeves, B. D.; Reynolds, J. R. *J. Mater. Chem.* **2003**, *13*, 2422.
(41) Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559.
(42) Balan, A.; Gunbas, G.; Durmus, A.; Toppare, L. *Chem. Mater.* **2008**, *20*, 7510.
(43) Invernale, M. A.; Seshadri, V.; Mamangun, D. M. D.; Ding, Y.; Filloramo, J.; Sotzing, G. A. *Chem. Mater.* **2009**, *21*, 3332.
(44) Li, M.; Sheynin, Y.; Patra, A.; Bendikov, M. *Chem. Mater.* **2009**, *21*, 2482.
(45) Li, M.; Patra, A.; Sheynin, Y.; Bendikov, M. *Adv. Mater.* **2009**, *21*, 1707.
(46) Thompson, B. C.; Kim, Y.-G.; McCarley, T. D.; Reynolds, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 12714.
(47) Wu, C. G.; Lu, M. I.; Chang, S. J.; Wei, C. S. *Adv. Funct. Mater.* **2007**, *17*, 1063.
(48) Chen, H.-Y.; Hou, J.; Hayden, A. E.; Yang, H.; Houk, K. N.; Yang, Y. *Adv. Mater.* **2009**, *22*, 371.
(49) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317.
(50) DuBois, C. J.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 1844.
(51) Beaujuge, P. M.; Vasilyeva, S. V.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2009**, *42*, 3694.
(52) Wu, C.-G.; Lu, M. I.; Tsai, P.-F. *Macromol. Chem. Phys.* **2009**, *210*, 1851.
(53) Nielsen, C. B.; Angerhofer, A.; Abboud, K. A.; Reynolds, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 9734.
(54) Unur, E.; Beaujuge, P. M.; Ellinger, S.; Jung, J.-H.; Reynolds, J. R. *Chem. Mater.* **2009**, *21*, 5145.
(55) Shi, P.; Chad, M. A.; Knott, E. P.; Thompson, E. J.; Liu\, D. Y.; Mei, J.; Dyer, A. L.; Reynolds, J. R. Adv. Mater. **2010**, ASAP, DOI: 10.1002/adma.201002234.
(56) Içli, M.; Pamuk, M.; AlgI, F.; Önal, A. M.; Cihaner, A. *Org. Electron.* **2010**, *11*, 1255.
(57) Bredas, J. L.; Chance, R. R.; Silbey, R. *Phys. Rev. B: Condens. Matter* **1982**, *26*, 5843.
(58) Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1121.
(59) Liou, G.-S.; Lin, H.-Y. *Macromolecules* **2008**, *42*, 125.
(60) Wang, H.-M.; Hsiao, S.-H. *Polym. Chem.* **2010**, *1*, 1013.
(61) Heinze, J. r.; Frontana-Uribe, B. A.; Ludwigs, S. *Chem. Rev.* **2010**, *110*, 4724.
(62) Audebert, P.; Miomandre, F. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2007; Vol. *1*.
(63) Doblhofer, K.; Rajeshwar, K. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel-Dekker: New York, 1998.
(64) Heinze, J. r.; Frontana-Uribe, B. A.; Ludwigs, S. *Chem. Rev.* **2010**, *110*, 4724–4771.
(65) Hwang, J.; Tanner, D. B.; Schwendeman, I.; Reynolds, J. R. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 115205/1.
(66) CIE **1986**.
(67) Wyszecki, G.; Stiles, W. S. *Color Science: Concepts and Methods, Quantitative Data and Formulae*; 2nd ed.; John Wiley and Sons: New York, 1982.
(68) *Electrochromism and Electrochromic Devices*; 1st ed.; Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R., Eds.; Cambridge University Press: Cambridge, U.K., 2007.
(69) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R., Eds. *Electrochromism: Principles and Applications*; Wiley−VCH: Weinheim, Germany, 1995.
(70) Schanda, J. D. In *Handbook of Applied Photometry*; DeCusatis, D. C., Ed.; Optical Society of America: New York, 1998.
(71) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563.
(72) Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3964.
(73) Fabretto, M.; Vaithianathan, T.; Hall, C.; Mazurkiewicz, J.; Innis, P. C.; Wallace, G. G.; Murphy, P. *Electrochim. Acta* **2008**, *53*, 2250.
(74) Yoshioka, Y.; Jabbour, G. E. In *Handbook of Conducting Polymers*; Third ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2007; Vol. *1*.
(75) Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394.
(76) Robinson, N. D.; Berggren, M. In *Handbook of Conducting Polymers*; Third ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2007; Vol. *1*.
(77) Steiger, J.; Heun, S.; Tallant, N. *J. Imaging Sci. Technol.* **2003**, *47*, 473.
(78) Yoshioka, Y.; Jabbour, G. E. *Synth. Met.* **2006**, *156*, 779.
(79) Kopola, P.; Tuomikoski, M.; Suhonen, R.; Maaninen, A. *Thin Solid Films* **2009**, *517*, 5757.
(80) Birnstock, J.; Blassing, J.; Hunze, A.; Scheffel, M.; Stossel, M.; Heuser, K.; Wittmann, G.; Worle, J.; Winnacker, A. *Appl. Phys. Lett.* **2001**, *78*, 3905.
(81) Argun, A. A.; Reynolds, J. R. *J. Mater. Chem.* **2005**, *15*, 1793.
(82) Hu, L.; Gruner, G.; Li, D.; Kaner, R. B.; Cech, J. *J. Appl. Phys.* **2007**, *101*, 016102.
(83) Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. *Adv. Funct. Mater.* **2007**, *17*, 3074.
(84) Zeng, W.; Wu, H.; Zhang, C.; Huang, F.; Peng, J.; Yang, W.; Cao, Y. *Adv. Mater.* **2007**, *19*, 810.
(85) Huh, J. W.; Kim, Y. M.; Park, Y. W.; Choi, J. H.; Lee, J. W.; Lee, J. W.; Yang, J. W.; Ju, S. H.; Paek, K. K.; Ju, B. K. *J. Appl. Phys.* **2008**, *103*, 044502/1.
(86) Mortimer, R. J.; Graham, K. R.; Grenier, C. R. G.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2269.
(87) Invernale, M. A.; Ding, Y.; Sotzing, G. A. *ACS Appl. Mater. Interfaces* **2010**, *2*, 296.
(88) Matyba, P.; Yamaguchi, H.; Eda, G.; Chhowalla, M.; Edman, L.; Robinson, N. D. *ACS Nano* **2010**, *4*, 637.
(89) Tehrani, P.; Isaksson, J.; Mammo, W.; Andersson, M. R.; Robinson, N. D.; Berggren, M. *Thin Solid Films* **2006**, *515*, 2485.
(90) Brotherston, I. D.; Mudigonda, D. S. K.; Osborn, J. M.; Belk, J.; Chen, J.; Loveday, D. C.; Boehme, J. L.; Ferraris, J. P.; Meeker, D. L. *Electrochim. Acta* **1999**, *44*, 2993.
(91) Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. *Adv. Funct. Mater.* **2007**, *17*, 3074.
(92) de Gans, B.-J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 203.
(93) Shim, G. H.; Han, M. G.; Sharp-Norton, J. C.; Creager, S. E.; Foulger, S. H. *J. Mater. Chem.* **2008**, *18*, 594.
(94) Small, W. R.; Masdarolomoor, F.; Wallace, G. G.; in het Panhuis, M. *J. Mater. Chem.* **2007**, *17*, 4359.
(95) Yu, J.; Abley, M.; Yang, C.; Holdcroft, S. *Chem. Commun.* **1998**, 1503.
(96) Gordon, T. J.; Yu, J.; Yang, C.; Holdcroft, S. *Chem. Mater.* **2007**, *19*, 2155.
(97) Admassie, S.; Inganas, O. *J. Electrochem. Soc.* **2004**, *151*, H153.
(98) Lidzey, D. G.; Pate, M. A.; Weaver, M. S.; Fisher, T. A.; Bradley, D. D. C. *Synth. Met.* **1996**, *82*, 141.
(99) Jager, E. W. H.; Smela, E.; Inganas, O. *Science* **2000**, *290*, 1540.
(100) Schanze, K. S.; Bergstedt, T. S.; Hauser, B. T. *Adv. Mater.* **1996**, *8*, 531.
(101) Renac, M. L.; Bazan, G. C.; Roitman, D. *Adv. Mater.* **1997**, *9*, 392.
(102) Melucci, M.; Favaretto, L.; Zanelli, A.; Cavallini, M.; Bongini, A.; Maccagnani, P.; Ostoja, P.; Derue, G.; Lazzaroni, R.; Barbarella, G. *Adv. Funct. Mater.* **2010**, *20*, 445.

(103) Beh, W. S.; Kim, I. T.; Qin, D.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 1038.
(104) Makela, T.; Haatainen, T.; Ahopelto, J.; Isotalo, H. *J. Vac. Sci. Technol., B* **2001**, *19*, 487.
(105) Tan, L.; Kong, Y. P.; Pang, S. W.; Yee, A. F. *J. Vac. Sci. Technol., B* **2004**, *22*, 2486.
(106) Choi, J.; Kumar, A.; Sotzing, G. A. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2007**, *44*, 1305.
(107) Li, G.; Martinez, C.; Semancik, S. *J. Am. Chem. Soc.* **2005**, *127*, 4903.
(108) Lim, J.-H.; Mirkin, C. A. *Adv. Mater.* **2002**, *14*, 1474.
(109) Jang, S.-Y.; Seshadri, V.; Khil, M.-S.; Kumar, A.; Marquez, M.; Mather, P. T.; Sotzing, G. A. *Adv. Mater.* **2005**, *17*, 2177.
(110) Dyer, A. L.; Grenier, C. R. G.; Reynolds, J. R. *Adv. Funct. Mater.* **2007**, *17*, 1480.
(111) Chandrasekhar, P.; Zay, B. J.; McQueeney, T.; Birur, G. C.; Sitaram, V.; Menon, R.; Coviello, M.; Elsenbaumer, R. L. *Synth. Met.* **2005**, *155*, 623.
(112) Nikolou, M.; Dyer, A. L.; Steckler, T. T.; Donoghue, E. P.; Wu, Z.; Heston, N. C.; Rinzler, A. G.; Tanner, D. B.; Reynolds, J. R. *Chem. Mater.* **2009**, *21*, 5539.
(113) Pozo-Gonzalo, C.; Mecerreyes, D.; Pomposo, J. A.; Salsamendi, M.; Marcilla, R.; Grande, H.; Vergaz, R.; Barrios, D.; Sanchez-Pena, J. M. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 101.
(114) Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* **2001**, *13*, 634.
(115) Zhao, L.; Zhao, L.; Xu, Y.; Qiu, T.; Zhi, L.; Shi, G. *Electrochim. Acta* **2009**, *55*, 491.
(116) Vasilyeva, S. V.; Unur, E.; Walczak, R. M.; Donoghue, E. P.; Rinzler, A. G.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2288.
(117) Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 1338.
(118) Tran-Van, F.; Beouch, L.; Vidal, F.; Yammine, P.; Teyssie, D.; Chevrot, C. *Electrochim. Acta* **2008**, *53*, 4336.
(119) Vidal, F.; Plesse, C.; Aubert, P.-H.; Beouch, L.; Tran-Van, F.; Palaprat, G.; Verge, P.; Yammine, P.; Citerin, J.; Kheddar, A.; Sauques, L.; Chevrot, C.; Teyssie, D. *Polym. Int.* **2010**, *59*, 313.
(120) Sindhu, S.; Rao, K. N.; Gopal, E. S. R. *Bull. Mater. Sci.* **2008**, *31*, 15.
(121) Schwendeman, I.; Hickman, R.; Soenmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3118.
(122) Sapp, S. A.; Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R. *Adv. Mater.* **1996**, *8*, 808.
(123) Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 2101.
(124) Padilla, J.; Otero, T. F. *Electrochem. Commun.* **2008**, *10*, 1.
(125) Takahashi, Y.; Hayashi, N.; Oyaizu, K.; Honda, K.; Nishide, H. *Polym. J.* **2008**, *40*, 763.
(126) Beaupre, S.; Breton, A.-C.; Dumas, J.; Leclerc, M. *Chem. Mater.* **2009**, *21*, 1504.
(127) Chandrasekhar, P.; Zay, B. J.; McQueeney, T.; Scara, A.; Ross, D.; Birur, G. C.; Haapanen, S.; Kauder, L.; Swanson, T.; Douglas, D. *Synth. Met.* **2003**, *135−136*, 23.
(128) Pages, H.; Topart, P.; Lemordant, D. *Electrochim. Acta* **2001**, *46*, 2137.
(129) Chandrasekhar, P.; Zay, B. J.; Birur, G. C.; Rawal, S.; Pierson, E. A.; Kauder, L.; Swanson, T. *Adv. Funct. Mater.* **2002**, *12*, 95.
(130) Tehrani, P.; Hennerdal, L.-O.; Dyer, A. L.; Reynolds, J. R.; Berggren, M. *J. Mater. Chem.* **2009**, *19*, 1799.
(131) Coleman, J. P.; Lynch, A. T.; Madhukar, P.; Wagenknecht, J. H. *Sol. Energy Mater. Sol. Cells* **1999**, *56*, 395.