

Completing the Color Palette with Spray-Processable Polymer Electrochromics

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ABSTRACT: The field of electrochromic polymers has now reached an important milestone with the availability of a yellow to fully transmissive, cathodically coloring, solution-processable electroactive polymer. This is in addition to previously published electrochromic polymers that have neutral state colors that span from orange, red, magenta, blue, cyan, green, and black, that also attain highly transmissive states upon switching. With this, the full color palette is now complete allowing the largest variety of colors for transmissive and reflective electrochromic display applications. Here, we report on how we have been able to obtain this full color palette through synthetic modifications and color tuning utilizing electron rich and donor–acceptor repeat units, electron-donating substituents, and steric interactions with our 3,4-alkylenedioxythiophene family of polymers. Additionally, using solubilizing pendant groups for both organic and aqueous compatibility, we have been able to create this color palette with fully solution processable materials, paving the way for materials patterning, printing, and incorporation into devices for display and window applications.

KEYWORDS: electrochromics, conjugated electroactive polymers, information displays, electrochromic windows, multicolor polymers



INTRODUCTION

When one considers the development of π -conjugated polymers for optoelectronic applications, such as polymer-based LEDs and photovoltaic systems, it is striking to see how many materials have been synthesized as researchers strive to develop a cohesive set of structure:property relationships and develop materials with optimized properties.¹ In the area of PLEDs, this has certainly proven successful as red, green, and blue light-emitting polymers are now well-developed, along with systems that emit white.^{2–4} In considering light-emitting polymers for display applications, these RGB emitters are necessary, as these colors are additive and their mixing allows any color of the spectrum to be generated,⁵ whereas white light-emitting polymers are especially useful for what one might consider more traditional lighting applications.

Turning our attention to the spectral properties of π -conjugated polymers being developed for organic photovoltaic (OPV) applications, a balance is struck between systems with broad light absorption properties that span from the ultraviolet, through the visible, and into the near-infrared (in order to capture the broadest amount of the solar flux possible). At the same time, establishing the position of the HOMO and LUMO levels plays a strong role in determining the open circuit voltage of the cell and ability of the photoexcited polymer to transfer an electron to an electron acceptor.⁶ Although most solar applications merely require broad light absorption, there are opportunities available for aesthetically pleasing solar cells where the absorptive or reflective color of the active material can play a role in the visible image of the ultimate device. As just one example, we have produced green colored solar polymers with the goal of developing a series of green and brown colored materials that will allow solar cells to be viewed as natural vegetation mimics.^{7–9}

We have had the opportunity to carry out an extensive program in the development of conjugated polymers for electrochromic applications. In general, electrochromism (EC) involves the process of changing the absorption profile of a material with application of an electric field or passing of electrical charge. EC materials are exemplified by thin films of electroactive metal oxides (e.g., WO_3), soluble molecular electrochromes (e.g., viologens), and π -conjugated polymers. Those interested in reading more on these materials in general are directed to the several excellent reviews in the literature that have been published over recent years.^{10–14}

To serve as an effective electrochrome, these materials need to exhibit a certain set of properties. First and foremost, the absorption profile must present the desired color in its extreme redox states. Next, an easily accessible redox process is required in order to switch the electrochrome between these two states. Typically, these electrochemical processes must be induced at sufficiently low potentials to allow for many switches (on the order of thousands to millions) with little degradation. Finally, the material must exhibit processing and handling properties that allow it to be incorporated into the device architectures of interest.^{15,16}

Over the years, there has been continuous development in the area of ECPs. Starting with electrochemical polymerization, thin films of redox switchable polymers were shown to exhibit the EC phenomenon. Early work often led to what has become known as “multi-colored ECPs” that switched between two distinct colored states.¹⁷ Although these materials have been of strong scientific interest, useful applications of ECPs in windows and displays require that the polymer switches from one color state to

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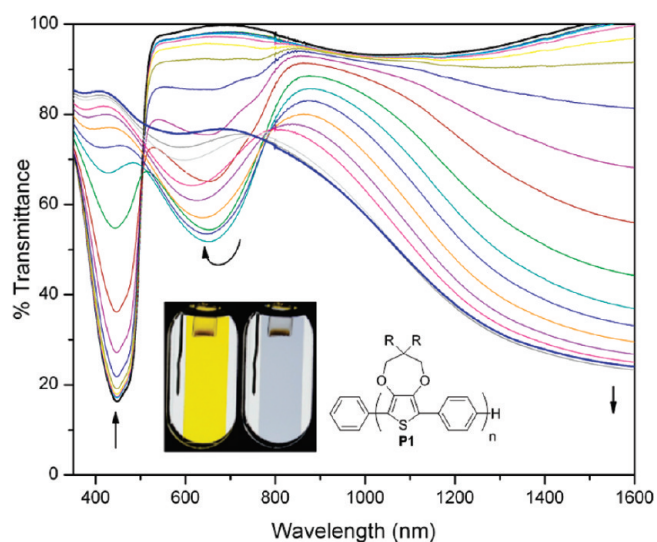


Figure 1. Spectroelectrochemical series for a spray-cast film of ECP-yellow on an ITO/glass electrode. Applied potentials were in the range from 0.18 to 1.08 V vs Fc/Fc⁺ at 50 mV step increments. The arrows show the direction of transmittance increase/decrease as the applied potential is increased. The inset shows photographs of the film in the extreme states and the polymer repeat unit structure. Reproduced with permission from ref 19. Copyright 2011 The Royal Society of Chemistry.

an essentially colorless and transmissive state. The multicolored ECPs are lacking in fulfillment of this requirement rendering them ineffective for these applications.

With all of this in mind, it is our distinct pleasure to be able to report that we have now “completed the color palette” with a series of soluble and spray processable ECPs, each of which can be switched to a highly transmissive state over many cycles. It is the intent of this Spotlight Article to provide a highlight of the process we have undergone in developing these polymers. Certainly, other groups have made strong contributions to the development of colored to transmissive ECPs that are solution processable as previously reviewed.^{15,16,18} It is not the intent of this article to present a comprehensive review as we have reported on previously, but more to tell the story of the process that was undergone in developing this particular set of ECPs.

■ YELLOW ECP COMPLETES THE COLOR PALETTE

This article is motivated by our recent report of the first cathodically coloring, vibrant yellow ECP that switches to a highly transmissive state upon oxidation.¹⁹ Although the chemical repeat unit for this polymer, as shown by ECP-yellow in Figure 1, is somewhat simple, being composed of alternating alkoxy-substituted 3,4-propylenedioxythiophene (ProDOT) and unsubstituted *p*-phenylene linking units, its easily accessible redox switching behavior was initially a bit surprising.

In an early application of the Grignard metathesis polymerization methodology, our group showed how dialkoxy substituted phenylenes could be linked with 3,4-ethylenedioxythiophene (EDOT) and was able to attain an ECP that switched from red to blue.²⁰ As such, we initially expected ECP-yellow to have a somewhat higher oxidation potential (making it less stable to repeated redox switching) and we expected a more orange color. This is not the case, as illustrated by the spectroelectrochemical series in Figure 1 that is presented in the form of percent transmission through the entire visible and into the near-infrared (NIR). It can be seen that the

neutral polymer film spectrum is dominated by a deep absorbance at 455 nm as illustrated by a minimum in the transmittance, along with an onset of absorption at 520 nm, which corresponds to an electronic bandgap of 2.38 eV. This deep absorption of blue light then provides the film with the vibrant yellow color shown in the photograph of the sprayed film on an ITO/glass slide in a cuvette in the figure inset.

Cyclic voltammetry shows this polymer to have an $E_{1/2}$ of +0.6 V vs Fc/Fc⁺, while differential pulse voltammetry indicates an onset for oxidation at +0.55 V vs Fc/Fc⁺. This potential for oxidation is somewhat higher than most of the other ECPs developed in our laboratory, but certainly is in the range for practical utility. Stepwise oxidation of the polymer leads to an initial absorption that peaks at 650 nm and is attributed to the polaronic state in the polymer. Importantly for electrochromic applications, this transition is subsequently bleached at a higher potential and thus the fully oxidized form of the polymer has the spectrum represented by the dark blue line shown in Figure 1 with a strong NIR absorbance attributed to the bipolaronic charge carrier. The fact that this form of the polymer attains >80% *T* through the full visible region causes the thin film to be highly transmissive sky blue.

■ FULL COLOR PALETTE

Having the ECP-yellow on hand now allows us to use Figure 2 as a means of teaching our ability to access the full palette of colors in ECPs that all switch to a highly transmissive state through a cathodically coloring process. This figure demonstrates the yellow, orange, red, magenta, blue, cyan, and green polymers by showing their repeat unit structures, photographs in their neutral colored and oxidized transmissive states, along with the visible spectra of the neutral forms.¹⁶ A simple red-shift of the $\pi-\pi^*$ transition is induced by removal of the *p*-phenylene unit in ECP-yellow, along with the use of two 2-ethylhexyloxy groups on the thiophene as opposed to the propylenedioxy bridge. This highly electron-rich polymer has sufficient interactions between the side chains to position its λ_{\max} at 490 nm providing ECP-orange.²¹ A random copolymerization of this bis-ethylhexyloxythiophene with dimethoxythiophene results in a copolymer with relaxed steric interactions compared to ECP-orange because of the smaller size of the methoxy substituents. This reduced steric interaction leads to a red shift of the λ_{\max} of ECP-red to 527 nm, and the polymer is deep red in color.²¹

Of the ECPs that we have developed, the disubstituted PProDOTs have proven to be the most versatile for developing our spray coating capabilities and long-lived devices. As such, the University of Florida has taken out a trademark on this family of ECPs known as SprayDOTs. The development of the PProDOT family allowed us to determine the effect of the chemical composition and size of the side chain on electrochromism. Starting with the dimethyl derivative, electrochemical polymerization was required to provide useful ECP films. The utilization of butyl substituents and a Grignard metathesis polymerization methodology provided relatively low molecular weight polymers that could be solution processed.²² Subsequently moving to dihexyl, and then longer chain alkoxy substituents, led to an increased solubility and ability to process by air brush spraying. A direct comparison by our group between long chain linear alkoxy and branched ethylhexyloxy derivatives led to an optimization of the EC properties as exhibited by the branched PProDOT-(CH₂OEtHx)₂, which in fact gained the nickname of SprayDOT-classic because of our ability to scale the synthesis of the polymer in a highly reproducible manner to provide a high-performance ECP.²³ The spectrum of this polymer is shown in Figure 2 as

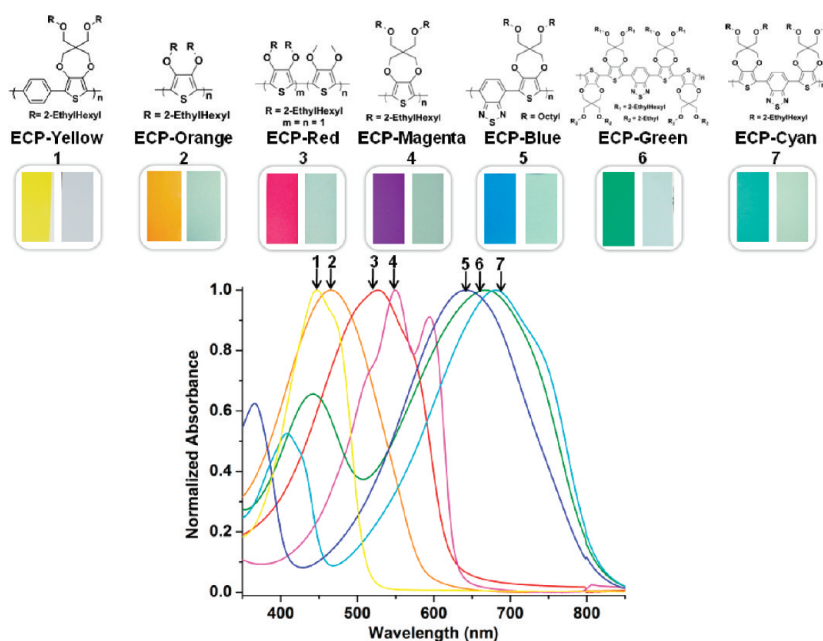


Figure 2. Repeat unit structures (top) and photographs of spray-cast polymer films in the neutral colored, and oxidized transmissive states. Normalized absorption spectra of neutral spray-cast polymer films (bottom) of P1–P7. Adapted with permission from ref 16 Copyright 2010 American Chemical Society.

ECP-magenta. The as-cast films are red in color with little absorption at wavelengths longer than 600 nm. Redox switching of these films between their neutral and oxidized states leads to an electrochemical annealing resulting in a 20 nm red-shift in the spectrum and the material is converted into a more deep purple/magenta color. This annealing effect can be attributed to polymer chain extension in the fully oxidized form as the polaronic and bipolaronic charge carriers are delocalized along the backbone. Subsequent reduction of the oxidized form leaves the polymer chains in their more extended conformations and thus the longer wavelength absorbance.

The electrochemical stability of these ProDOT polymers has allowed us to examine the long-term switching characteristics of both EC window and EC display-type device architectures. In one reflective-type device we demonstrated a high level of EC stability by switching PProDOT-Me₂ 180,000 times over the period of one week with only an 8% loss in reflective contrast in the NIR.²⁴ It should be noted that most of the device studies carried out to date have been performed on platforms developed with little focus toward encapsulation and exclusion of moisture and oxygen from the film. In a recent study, we have collaborated with the group of Professor Sam Graham (Georgia Institute of Technology) using a double polyisobutylene encapsulation method with an inert gas buffer.⁵⁶ EC windows constructed using ECP-magenta were shown to retain 94% of their original contrast after exposure to 50 °C and 80% relative humidity over a period of 40 days. These long-term switching and accelerated testing experiments, albeit still in the early stages, are quite encouraging for the ultimate development of practical ECDs.

In terms of chemical composition, the development of donor–acceptor (DA) polymers has had an immense impact on the development of π -conjugated polymers for applications ranging from transport (field effect transistors), photodetectors and photovoltaics (solar cells), and light-emission (polymer LEDs).^{25–27} The same can be said for our development of this family of ECPs. The DA methodology involves linking together electron donors and acceptors along the conjugated polymer chain such that the majority of the HOMO character of the

polymeric chromophore is contributed by the donor moiety while the LUMO is mainly contributed by the acceptor.¹⁸ As such, the HOMO–LUMO gap is easily probed via the oxidation and reduction properties of the donor and acceptor units, respectively. The perfectly alternating copolymerization of ProDOT with benzothiadiazole (BTD) leads to a polymer with 2-band absorption characteristics and a strong transmission window near 425 nm as illustrated for ECP-blue in Figure 2.²⁸ This polymer was synthesized using an inverted Suzuki coupling methodology,²⁹ and we found the optimized EC properties were attained using *n*-octyl substituents. The resulting polymer is a brilliant blue in the neutral state with a highly transparent, near colorless, oxidized state, being one of only a few organic solvent-processable blue electrochromic polymers available.

In moving from the alternating copolymer where there is a 1:1 ratio of the ProDOT and BTD to the more electron-rich composition containing 2:1 ProDOT to BTD, the slight raising of the HOMO level leads to a decrease in the energy of the bandgap and position of the window of transmission of the polymer relative to ECP-blue. Moving this window of transmission to 470 nm leads to a greening in the color as illustrated by the spectrum for ECP-cyan.³⁰ This polymer was prepared by first synthesizing the bis-ProDOT BTD trimeric monomer, which was then subsequently polymerized by oxidative polymerization methods. These oxidative polymerizations are most often accomplished using FeCl₃ as an oxidant, though other nonmetal containing oxidants, such as nitrosonium salts, can be employed. By increasing the electron-rich character of the polymer even further, via polymerization of a pentameric monomer yielding a polymer with a 4:1 ratio of ProDOT to BTD (ECP-green), led to a shift of the window of transmission to 507 nm and the formation of a family of green ECPs.³⁰

It is said that a picture is worth a thousand words. With this in mind, the end result of this work on these vibrantly colored polymers is illustrated by the photograph of a set of our ECPs in solution with varied concentrations in Figure 3.

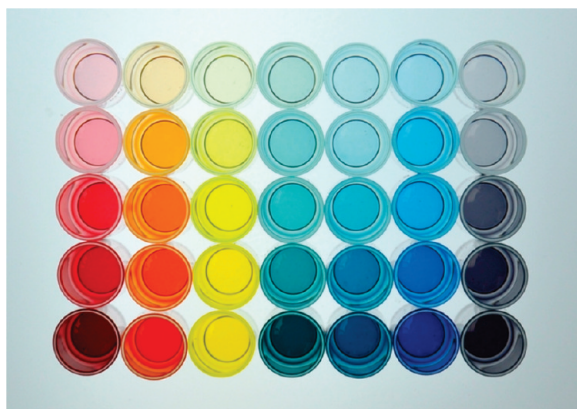


Figure 3. Photograph of solutions, illuminated from underneath, containing (from left to right) ECP-magenta, -orange, -yellow, -green, -cyan, -blue, and -black, proceeding from top to bottom at increasing concentrations.

COLORIMETRY AND COLOR ANALYSIS OF ECPs

Although the UV–vis–NIR spectra provide a full characterization of the electronic transitions that are present in these conjugated polymers, their application as electrochromic materials in displays and windows is a function of the color states induced. As such, colorimetry,^{5,31} and a full analysis of the color changes that occur as the polymer switches from its neutral to its oxidized state, is most important in determining their applicability. We have developed methodologies for colorimetric analysis for ECP films using standardized white light sources and commercial colorimeters.³²

There are two leading color spaces developed by the International Commission on Illumination (CIE) used for quantifying the color of objects; the 1931 xy chromaticity diagram and the 1976 $L^*a^*b^*$ color space. Although the xy chromaticity diagram is the color space of choice for emissive device color characterization, as it provides a method to allow prediction of ultimate colors upon mixing of light sources, it does not provide an intuitive understanding of relative color differences upon transmission or reflection. Whereas the xy chromaticity diagram is spatially nonuniform in representation of color differences, that of the $L^*a^*b^*$ color space is. The L^* , a^* , and b^* values also have the added benefit of being intuitive in predicting color as they are presented in a manner similar to how our brains process color stimuli. According to opponent color theory, these original signals received are converted to three opponent signals being an achromatic (light/dark) signal, a red-green signal, and a yellow-blue signal.³³ Similarly, the $L^*a^*b^*$ color space is presented with L^* as an optically linear measurement of the lightness (0 = black, 100 = diffuse white), a^* is a red-green balance ($+a^*$ = red and $-a^*$ = green hues), and b^* is a yellow-blue balance ($+b^*$ = yellow and $-b^*$ = blue). This results in a 3D representation of the color with the most common method of presentation similar to that shown in Figure 4 with the colors presented as a plot of the a^*b^* values.

Because of the uniformity of the $L^*a^*b^*$ color space, it is the primary color space used in industry for color comparison of reflective color surfaces and therefore the color space utilized in our group. Examination of the a^* and b^* values for the polymers in Figure 4 shows their color vibrancy in the neutral state by their distance from the origin. As the potential is stepped more positively, and the polymers transition to their bleached states,

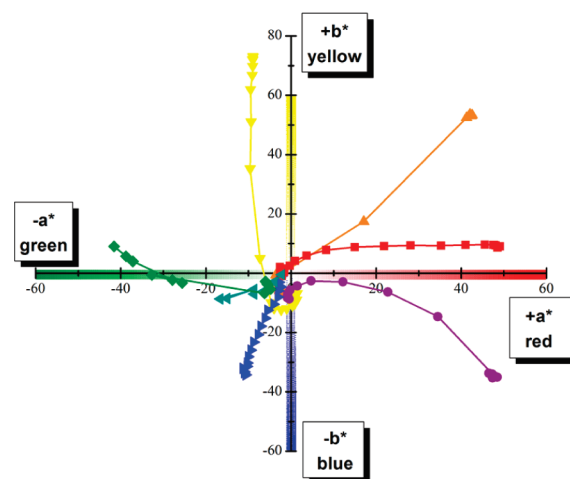


Figure 4. CIE 1976 a^*b^* color coordinates showing calculated values of the seven vibrantly colored ECPs (orange triangle, ECP-orange; red square, ECP-red; purple circle, ECP-magenta; blue right-facing triangle, ECP-blue; teal left-facing triangle, ECP-cyan; green, diamond, ECP-green; and yellow downward-facing triangle, ECP-yellow) as a function of applied potential. The polymer neutral states are furthest from the origin and the values track toward the origin as the polymer is oxidized to the bleached state.

the a^* and b^* values are reduced in magnitude as the saturation of the color is reduced to a more achromatic state.

As can be seen, we have been able to complete the four legs of the $L^*a^*b^*$ color space in addition to mixed color states exhibited by individual polymers, such as magenta (a color comprising a mixture of red and blue), orange (a color comprising a mixture of yellow and red), and cyan (a color comprising a mixture of green and blue).

ON DEVELOPING BLACK TO TRANSMISSIVE SWITCHING ECPs

Many applications in which ECPs are being considered for development would be best served by access to a material that could switch from a deep and highly absorbing black to colorless and transparent. Examples of these are architectural and automotive windows, where the lack of any one specific hue or chroma would not change the observer perception of the viewed area as the window tinted. In addition, the applicability of ECPs to e-readers and electronic paper would be greatly enhanced by access to such systems. As a black ECP would effectively and strongly absorb light from 400 to 750 nm, and the polymeric electrochromes outlined in Figure 2 have absorbances that span this entire region, it was realized that a black to transmissive ECP could be developed by random incorporation of specific chromophores along the polymer chain. We first reported this using a combination of our PProDOT homopolymers (strong magenta in color) in combination with our D–A ProDOT-BTD systems, such as ECP-cyan, that has a window of transmission occurring at the wavelength of maximum absorption of ECP-magenta, while at the same time absorbing both the red and blue portions of the visible spectrum effectively.³⁴ A random copolymerization of the ECP-cyan trimer with the ECP-magenta monomer in a 1:4 ratio led to a copolymer with a 1:6 overall BTD-to-ProDOT composition and random incorporation of 2, 3, 4, 5, 6, etc., runs of ProDOT interspersed between BTD units. With this structure, a

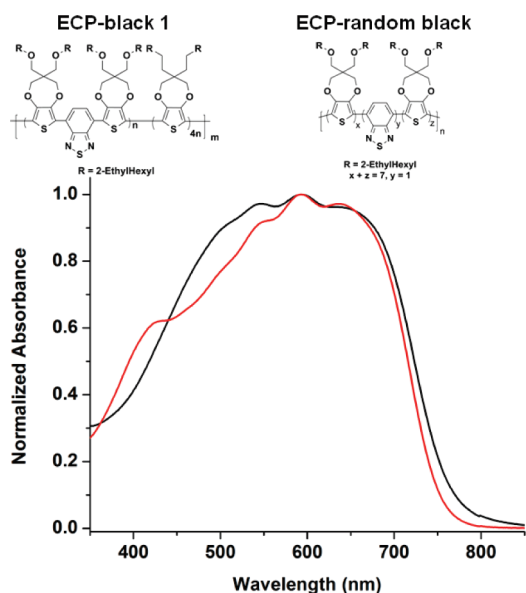


Figure 5. Absorbance spectra of thin films of ECP-black 1 (red line) and ECP-random black (black line), in their fully neutralized states. Adapted with permission from ref 35. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

fully black ECP was attained having a highly electron rich character and ability to switch to a highly transmissive form. This broadly absorbing neutral state is illustrated by the spectra in Figure 5 by ECP-black 1.

As noted earlier, although the ECP-blue contains one BTD per ProDOT, it still switches to a fully transmissive form. With this in mind, we developed a fully random polymerization to prepare a second form of ECP-black, which is identified by the name ECP-random black.³⁵ This polymer has a somewhat more random repeat unit structure than that of our initial ECP-black and, as can be seen in the comparative spectra in Figure 5, provides a broader and more reproducible visible absorbance spectrum, having a higher absorption in the range from 450 to 550 nm. This results in a polymer that has a rather achromatic neutral state compared to ECP-black 1. As ECP-black 1 exhibits a bit less absorption in the blue region of the spectrum, it has a slight bluish-purple tint for thin films of the polymer. On the other hand, ECP-random black transitions from a black through gray for decreasing film thicknesses and solution dilutions as shown in Figure 3 for the photographs of solutions of increasing dilutions. This can be further seen in Figure 6 for the three-dimensional $L^*a^*b^*$ plot for the neutral and oxidized states of ECP-random black. As thin films of this polymer switch from achromatic black to a rather achromatic transmissive state, the a^*b^* values cluster close to the origin while the largest contrast is in the L^* , or lightness, values.

MORPHOLOGY OF SPRAY-PROCESSED FILMS

Although most optoelectronic applications of π -conjugated polymers, including PLEDs and OPVs, require thin dense films with strong interchain interactions, this is not the case for electrochromism. In fact, due to the need to have these polymers swollen with solvent and able to be intercalated with electrolyte ions, an open-type morphology is desired. As such, we find solution spraying, using commercially available airbrush sprayers, to be quite convenient for processing in the laboratory.²³

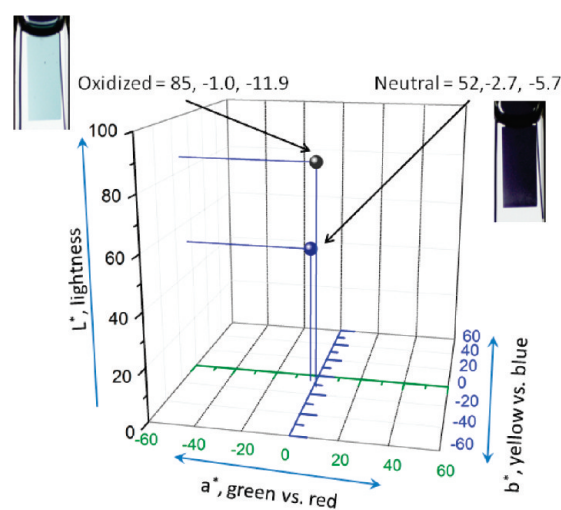


Figure 6. Three-dimensional $L^*a^*b^*$ plot of values measured for the fully neutralized (blue dot) and fully oxidized (black dot) states for ECP-random black at applied potentials of -0.2 and 0.8 V vs Ag/Ag^+ and photographs of the polymer film in the respective extreme states.

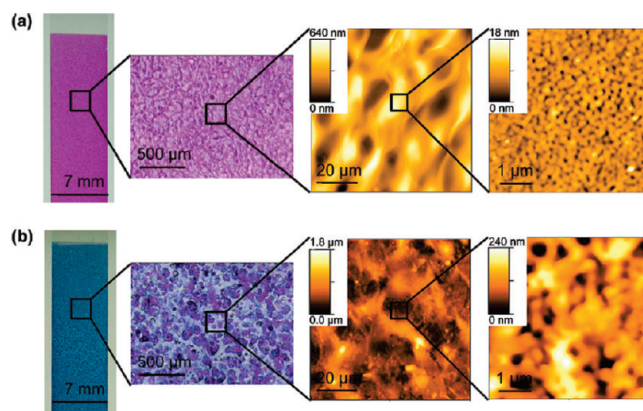


Figure 7. Morphology of spray-processed films of two different ProDOT polymers, PProDOT- Hx_2 (top) and PProDOT-(2-MeBu)₂ (bottom), illustrating how the morphology evolves when viewing large areas (far left photograph) to increasingly smaller areas using optical micrographs (second from left), and AFM images (two right micrographs) at smaller length scales. Scale bars are included in the image and AFM scan height is indicated in upper left scale bars. Adapted with permission from ref 41. Copyright 2010 American Chemical Society.

As one considers further development of these materials for industrial application, other methods such as gravure printing, screen printing, and inkjet printing, among others, are also likely to be employed.^{36–40} In considering the development of the morphology of a spray-processed film, one must bear in mind various length scales. This is illustrated in Figure 7, for two PProDOTs with different solubilizing groups.⁴¹ As evident from the photograph of the film on ITO glass on the left-hand side of the figure, the colors of the two polymers are distinctly different as-sprayed. As noted earlier, this probably speaks to the local organization of the polymer chains as the films are prepared and is of little impact to the overall properties of the polymers after they are redox switched. Of more importance are the nodular deposits that develop during spraying that are evident in the optical micrographs in the second set of images in the figure.

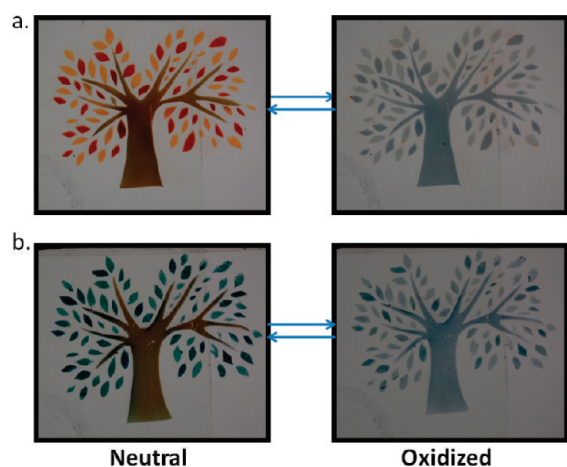


Figure 8. Patterned films of various polymers created by spray-casting through a shadow mask onto ITO/glass electrodes. The photographs on the left are of the polymer films on the electrodes as immersed in a TBAPF₆/PC electrolyte when neutralized (left) and upon oxidation (right). Adapted with permission from ref 21. Copyright 2010 American Chemical Society.

Here it can be seen that the bottom polymer is developing a rougher morphology than that of the top, which is forming a more continuous film on the ITO. This relative smoothness on the top film is evident in examining the first set of atomic force microscopy (AFM) images that show the 20 μm scale bar. At this dimension, it is evident that the top polymer is presenting a smoother overall morphology and the bottom polymer is significantly rougher, as evidenced by the z-direction scale bar, with the top image presented with a 640 nm scale and the bottom image in a 1.8 μm scale. This is likely due to lower solubility of the bottom polymer, which precipitates more rapidly upon spraying, and drying of the volatile solvent, toluene. In carrying out these analyses, one must be careful to try to understand the changes in morphology at all possible dimensions. This is further shown in the last set of AFM images at the highest magnification showing the 1 μm scale bar. While both images have high and low regions across the film, the ranges of the scales (18 nm for the PProDOT-Hx₂ film and 240 nm for the PProDOT-(2-MeBu)₂ film) further supports the conclusion that a rougher, open morphology is desired for polymer electrochromic applications as the porosity of the polymer film at this scale is especially important as one considers the need to have solvent and electrolyte penetrating the film, leading to the ability to rapidly and fully switch the polymers between their extreme states.

■ PATTERNING OF ECPs

The ECPs we have developed are solution processable from common volatile organic solvents with the current method of deposition being spray casting, as noted earlier. Patterning of the electrochromic films is then performed by spraying the ECP solution through a shadow mask applied to the electrode surface, leaving the area to be patterned exposed. By use of these methods, various patterned ECP films have been created with large-scale features as shown in Figure 8 for the patterned trees sprayed onto ITO/glass electrodes.²¹ The leaves of the “Fall” tree (a) were created by spraying the polymers, ECP-red and ECP-orange sequentially through a mask adhered to the electrode surface. The leaves of the “Spring” tree (b) were created using the polymers ECP-green, ECP-cyan, and ECP-blue. In both

instances, bleaching of the colors upon oxidation leads to similarly colored “Winter” trees.

Other simple patterns have been created including text and geometric designs. By masking off different areas of the pattern during spray casting, multicolored, layered films are possible, demonstrated by the color of the trunks of the trees in Figure 8, where the color brown was created by use of green, orange, and red polymer layers. This concept is further illustrated in the later section on subtractive color mixing. As this method is effective for creating simple patterns on dimensions as low as several millimeters, there remains potential for processing and patterning utilizing higher throughput industrial printing methods where fine, more intricate patterns with even higher resolution are desired.

■ WATER SOLUBILITY AND POSSIBILITY OF ORTHOGONAL SOLVENT PROCESSING

As the full color palette of solution-processable electrochromic polymers has been developed, our focus has recently been directed toward recreating this success with materials that offer an added advantage of lower environmental impact during processing. Although vibrantly colored, visibly homogeneous thin films can be easily sprayed from volatile organic solvents such as toluene, chloroform, and dichloromethane, these solvents and the volumes required are not desirable for industrially relevant processing methods that would be employed for larger scale applications.

To this end, we have developed methods that allow for synthesis and workup of conjugated polymers under typical organic conditions followed by defunctionalization to yield polymers processable from water.⁴² Maintaining the organic solubility during polymerization and characterization is desirable as it allows for use of known and optimized reaction conditions followed by well-established purification (precipitation and solvent extraction) and characterization methods (NMR, IR, GPC, HPLC) used in many organic polymer chemistry laboratories in academia and industry. We have found that by using the desired polymer backbone, while changing the organic solubilizing alkyl or alkoxy substituents to long alkyl chain ester substituents, the final sprayed polymer film color (spectra and colorimetry) is little changed. These derivatives bring the added benefit of being reactive to defunctionalization, with chemical or thermal cleavage of the ester groups leading to either alcohol or carboxylic acid substituted polymers.⁴³ This is illustrated by the saponification in Figure 9, where we have utilized the ECP-blue polymer backbone (alternating ProDOT and BTB units) with alkyl-ester solubilizing groups, allowing for the polymer to be isolated and purified using common organic solvents and precipitation.^{28,44} Treating the polymer with a concentrated basic alcohol solution defunctionalizes the ester to yield a polyionic salt. In further work utilizing the ECP-magenta backbone, we have produced a fully water-soluble polymer after defunctionalization to yield a material that is then processable from water or alcohols using a variety of methods, such as drop-casting and spin-coating, along with the before-mentioned spray processing.⁴⁴

As shown in the series of photographs in the bottom of Figure 9, the alkyl-ester is soluble in organic solvents (chloroform shown here) and upon conversion to the polyion, the polymer is no longer soluble in the organic solvent. Further treatment of the processed polymer film with an acid (e.g., toluene sulfonic acid) converts the ionic functionalities to carboxylic acids where the polymer is insoluble in water and organic solvents. This provides an added benefit when considering the possibility of multilayer printing where

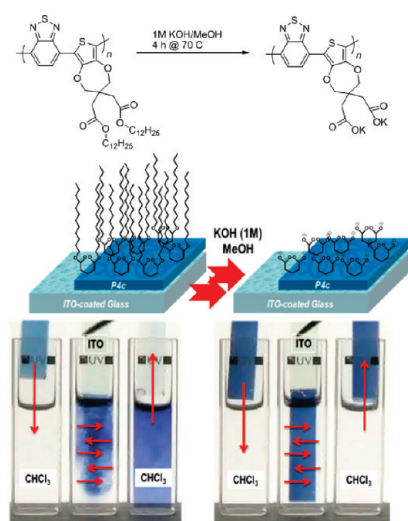


Figure 9. Schematic (top) of chemical defunctionalization of an organic soluble alkyl-ester ECP to an insoluble polyion. Drawing (middle) and photographs (bottom) demonstrating the defunctionalization process. Reproduced with permission from ref 28. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

processing stacked layers sequentially from orthogonal solvents is possible in addition to polymers switchable in aqueous solvents.^{45,46}

■ RAPIDLY SWITCHING ECPS: THE STORY OF ORGANIC AND AQUEOUS COMPATIBILITY

In addition to color vibrancy, transmissive states, and processability, one of the important aspects to consider for electrochromics is switching speed. Although there are many applications that require rapid switching speeds, which we define here as the time to reach the desired state (transmissive or colored), the definition of what is rapid is rather arbitrary and subjective. Those looking for video displays define rapid as being on the order of 30 ms–50 ms, while applications such as information displays, e-readers, and point-of-purchase advertising typically target the 100 to 500 ms range. Yet, in many electrochromic windows applications, what is defined as “fast” in the previous applications is not necessary and could even be undesirable.

Although the descriptor may be arbitrary (fast, rapid, quick, high-speed), the method to characterize is not. Previously, we have defined the characterization methods to utilize when establishing polymer film switching speed or rate at which it reaches the extreme states.¹⁶ In utilizing those methods, we have established the switching speeds for a series of our polymers, with ECP-green, exhibiting one of the faster switches (while maintaining a high contrast) as shown in Figure 10a. When switched in an alkylammonium/propylene carbonate electrolyte (1 M TBABF₄ in PC), the polymer exhibits a contrast of 48% at 670 nm when each extreme potential is held for 10 s. It can be seen that little contrast is lost with the polymer maintaining a 43% contrast when switched with 0.5 s switching times.

Currently underway in our group is research directed to establishing how fast these polymers switch when electrolyte ionic conductivity is taken into consideration and optical instrumentation is able to record rapidly (measurement times of 10 ms or less). As mentioned, ionic conductivity of the electrolyte is an important factor in allowing the electrochromic material to reach its most rapid switch speed. While there are many organic

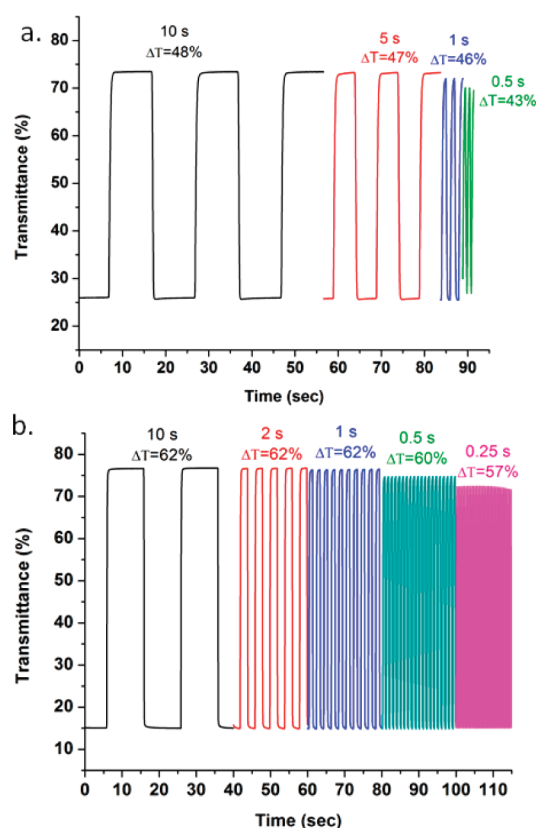


Figure 10. Switching rates of (a) ECP-green in 1 M TBABF₄/PC measured at 670 nm and (b) PProDOT-diacid in 1 M KNO₃/H₂O measured at 575 nm, sprayed onto ITO/glass electrodes monitored as a function of percent transmittance over time at increasing switch speeds. Adapted with permission from ref 44. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

electrolytes of high ionic conductivity (e.g., 6.8 mS/cm for 1 M TBABF₄/PC, 5.0 mS/cm for 1 M LiBTI/PC), and much focus has been toward ionic liquids as high ionic conductivity electrolytes (e.g., 8.8 mS/cm for EMI-BTI and 27.0 mS/cm for EMI-DCA at room temperature) aqueous electrolytes remain as those with the highest ionic conductivity. Although aqueous electrolytes have a narrow electrochemical window compared to the organic electrolytes, and especially the ionic liquids, the voltage range in which the electron rich electrochromic polymers we have developed are optically active is well within the stability window of aqueous electrolytes. As is seen in Figure 10b, the combination of a high ionic conductivity aqueous electrolyte (1 M KNO₃/H₂O with a room temperature ionic conductivity of 87.3 mS/cm) and the presence of protic polar carboxylic acid functional groups that have a greater affinity for the electrolyte, results in films that maintain a high contrast at even faster switch rates.⁴⁴

Although the spray-processed polymer has a relatively high transmittance contrast of 62% at relatively long switch times (i.e., 10 s), the contrast only drops by 8% when the switch time is decreased to 250 ms. As the variety of functional groups appended to the backbone of the current color palette of ECPS is expanding, the ability to tune compatibility with electrolytes of various conductivities is possible with the promise of even faster switch speeds as improved ion/solvent diffusion, penetration, and intercalation would allow charge balance to approach time scales on the order of that for charge injection.

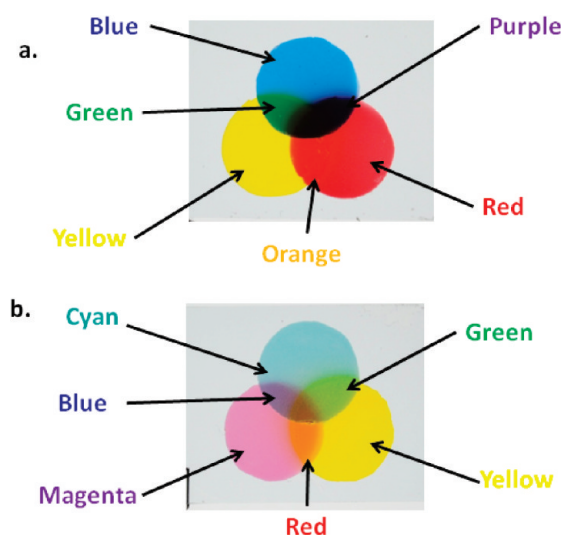


Figure 11. Spray-cast films on ITO/glass illustrating the subtractive color mixing concept as applied using electrochromic polymers. (a) The red-yellow-blue primaries where their overlaps create green, orange, and purple; and (b) the cyan-yellow-magenta primaries where their primaries create blue, red, and green. Reproduced with permission from ref 19. Copyright 2011 The Royal Society of Chemistry.

RYB AND CMYK SUBTRACTIVE COLOR MIXING

Subtractive color mixing is the theory used in mixing paints and other nonemitting color systems to create secondary colors; red plus blue makes purple, yellow plus blue makes green, etc. As has been utilized for decades in the printing industry, creating a large gamut of colors is possible using subtractive colors by printing with cyan, magenta, yellow, and “key” black (CMYK) inks. Subtractive color mixing operates on the principle of beginning with white light, and as an ink (or electrochromic polymer) is added to a surface, some of the white light is absorbed, filtered, or subtracted, from the original white light reflecting or transmitting a color. As more colors are added, the entirety of the white light can be absorbed, producing black. This is different than the concept of additive color primaries that are typically red, green, and blue, of which mixing combinations of these colors in emissive states, produces additive secondary colors. Unfortunately, some focus in the literature (including work from our group) about producing electrochromic materials sets that yield red, green, and blue primaries has provided confusion when considering these materials for nonemissive displays.^{20,30,47–55} Although these colors are relevant for emissive materials in the sense of being able to complete the color palette, this is not the case for electrochromics.

The attributes of subtractive color mixing theory can be demonstrated through Venn diagrams. When cyan and magenta mix, or overlap, they create blue; when yellow and magenta mix, they create red; when cyan and yellow mix, they create green; and finally, when cyan, magenta, and yellow mix, they create black. These mixtures, along with the above-mentioned red, yellow and blue combinations are seen in the Venn diagram in Figure 11 using overlapping films of our spray-processed ECPs.¹⁹ To widen the gamut, these secondary colors can be further mixed or a practice used in the printing industry, half-toning, can be utilized to create a saturation gradient or to create a full spectrum of colors. With this, a completed color palette can be realized utilizing the subtractive color primaries developed in our group

in a wide variety of ways including blending, overlapping layers, and lateral patterning methods. This is in addition to the color black, allowing for the largest variety of shades and tones currently available in electrochromic systems.

PERSPECTIVE ON THE FIELD

This Spotlight Article details a special point in a research program; specifically the accomplishment of a distinct set of goals. Here, we are able to review the complete development of a full set of cathodically coloring ECPs, which provide every color one would need for display applications along with black as desired for achromatic smart windows. With the full color palette achieved, one would ask what remains to be done from a materials perspective. Although the synthesis appears complete, work still remains in the areas of fine-tuning material performance (processability, color contrast, hue/saturation tunability, switching speed, redox/environmental stability, etc.) and solubility through structural modifications. As these polymers are all solution processable, they will also find application using a variety of processing techniques spanning spray-coating, roll-to-roll coating (e.g., slot-die), screen printing, and inkjet printing. Additionally, investigation of these polymers in device structures of varying complexity and applicability will allow for further understanding of the properties and potential of polymeric ECPs. The future is indeed bright and vibrant for these materials.

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REFERENCES

- (1) Skotheim, T. A.; Reynolds, J. R. *Handbook of Conducting Polymers*, 3rd ed.; CRC Press, Taylor and Francis Group: Boca Raton, FL, 2007.
- (2) Kobayashi, H.; Kanbe, S.; Seki, S.; Kiguchi, H.; Kimura, M.; Yudasaka, I.; Miyashita, S.; Shimoda, T.; Towns, C. R.; Burroughes, J. H.; Friend, R. H. *Synth. Met.* **2000**, *111–112*, 125–128.
- (3) Vulto, S. I. E.; Buechel, M.; Duineveld, P. C.; Dijkman, F.; Hack, M.; Kilitziraki, M.; de Kok, M. M.; Meulenkaamp, E. A.; Rubingh, J.-E. J. M.; van de Weijer, P.; de Winter, S. H. *Proc. SPIE-Int. Soc. Opt. Eng.* **2004**, *5214*, 40–49.
- (4) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. *Adv. Mater.* **2010**, *22*, 572–582.
- (5) Wyszecki, G.; Stiles, W. S. *Color Science: Concepts and Methods, Quantitative Data and Formulae*, 2nd ed.; Wiley-Interscience: New York, 2000.
- (6) Thompson, B. C.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.
- (7) Beaujuge, P. M.; Subbiah, J.; Choudhury, K. R.; Ellinger, S.; McCarley, T. D.; So, F.; Reynolds, J. R. *Chem. Mater.* **2010**, *22*, 2093–2106.

- (8) Subbiah, J.; Beaujuge, P. M.; Choudhury, K. R.; Ellinger, S.; Reynolds, J. R.; So, F. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1154–1158.
- (9) Subbiah, J.; Choudhury, K. R.; Ellinger, S.; Reynolds, J. R.; So, F. *IEEE J. Sel. Top. Quantum Electron* **2010**, *16*, 1792–1800.
- (10) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*; Cambridge University Press: New York, 2007.
- (11) Mortimer, R. J. *Annu. Rev. Mater. Res.* **2010**, *41*, No. DOI: 10.1146/annurev-matsci-062910-100344.
- (12) Baetens, R.; Jelle, B. P.; Gustavsen, A. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 87–105.
- (13) Granqvist, C. G. *Oxide-Based Electrochromics*; John Wiley & Sons: New York, 2010; pp 325–341.
- (14) Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, *27*, 2–18.
- (15) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268–320.
- (16) Amb, C. M.; Dyer, A. L.; Reynolds, J. R. *Chem. Mater.* **2011**, *23*, 397–415.
- (17) Dyer, A. L.; Reynolds, J. R. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2007; Vol. 1.
- (18) Beaujuge, P. M.; Amb, C. M.; Reynolds, J. R. *Acc. Chem. Res.* **2010**, *43*, 1396–1407.
- (19) Amb, C. M.; Kerszulis, J. A.; Thompson, E. J.; Dyer, A. L.; Reynolds, J. R. *Polymer Chemistry* **2011**, *2*, 812–814.
- (20) Wang, F.; Wilson, M. S.; Rauh, R. D.; Schottland, P.; Thompson, B. C.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 2083–2091.
- (21) Dyer, A. L.; Craig, M. R.; Babiarez, J. E.; Kiyak, K.; Reynolds, J. R. *Macromolecules* **2010**, *43*, 4460–4467.
- (22) Welsh, D. M.; Kloppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, *35*, 6517–6525.
- (23) Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559–7569.
- (24) Aubert, P.-H.; Argun, A. A.; Cirpan, A.; Tanner, D. B.; Reynolds, J. R. *Chem. Mater.* **2004**, *16*, 2386–2393.
- (25) Heeger, A. J. *Chem. Soc. Rev.* **2010**, *39*, 2354–2371.
- (26) Rasmussen, S. C.; Pomerantz, M. In *Handbook of Conducting Polymers*, 3rd ed.; CRC Press: Boca Raton, FL, 2007; Vol. 1.
- (27) Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985.
- (28) Amb, C. M.; Beaujuge, P. M.; Reynolds, J. R. *Adv. Mater.* **2010**, *22*, 724–728.
- (29) Zhang, M.; Tsao, H. N.; Pisula, W.; Yang, C.; Mishra, A. K.; Muellen, K. J. *Am. Chem. Soc.* **2007**, *129*, 3472–3473.
- (30) Beaujuge, P. M.; Vasilyeva, S. V.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2009**, *42*, 3694–3706.
- (31) Ohta, N.; Robertson, A., *Colorimetry: Fundamentals and Applications*; John Wiley & Sons: West Sussex, U.K., 2005.
- (32) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563–1571.
- (33) Berns, R. S. *Billmeyer and Saltzman's Principles of Color Technology*, 3rd ed.; John Wiley & Sons: New York, 2000.
- (34) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nat. Mater.* **2008**, *7*, 795–799.
- (35) Shi, P.; Amb, C. M.; Knott, E. P.; Thompson, E. J.; Liu, D. Y.; Mei, J.; Dyer, A. L.; Reynolds, J. R. *Adv. Mater.* **2010**, *22*, 4949–4953.
- (36) de Gans, B.-J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 203–213.
- (37) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753–1765.
- (38) Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394–412.
- (39) Birnstock, J.; Blassing, J.; Hunze, A.; Scheffel, M.; Stossel, M.; Heuser, K.; Wittmann, G.; Worle, J.; Winnacker, A. *Appl. Phys. Lett.* **2001**, *78*, 3905–3907.
- (40) Kopola, P.; Tuomikoski, M.; Suhonen, R.; Maaninen, A. *Thin Solid Films* **2009**, *517*, 5757–5762.
- (41) Mortimer, R. J.; Graham, K. R.; Grenier, C. R. G.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2269–2276.
- (42) Jiang, H.; Taranekar, P.; Reynolds, J. R.; Schanze, K. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 4300–4316.
- (43) Reeves, B. D.; Unur, E.; Ananthakrishnan, N.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 5344–5352.
- (44) Beaujuge, P. M.; Amb, C. M.; Reynolds, J. R. *Adv. Mater.* **2010**, *22*, 5383–5387.
- (45) Zakhidov, A. A.; Lee, J.-K.; Fong, H. H.; DeFranco, J. A.; Chatzichristidi, M.; Taylor, P. G.; Ober, C. K.; Malliaras, G. G. *Adv. Mater.* **2008**, *20*, 3481–3484.
- (46) Lee, J.-K.; Fong, H. H.; Zakhidov, A. A.; McCluskey, G. E.; Taylor, P. G.; Santiago-Berrios, M.; Abruna, H. D.; Holmes, A. B.; Malliaras, G. G.; Ober, C. K. *Macromolecules* **2010**, *43*, 1195–1198.
- (47) Unur, E.; Beaujuge, P. M.; Ellinger, S.; Jung, J.-H.; Reynolds, J. R. *Chem. Mater.* **2009**, *21*, 5145–5153.
- (48) Balan, A.; Baran, D.; Toppare, L. *J. Mater. Chem.* **2010**, *20*, 9861–9866.
- (49) Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Funct. Mater.* **2008**, *18*, 2026–2030.
- (50) Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Mater.* **2008**, *20*, 691–695.
- (51) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem.* **2004**, *43*, 1498–1502.
- (52) Sonmez, G.; Wudl, F. *J. Mater. Chem.* **2005**, *15*, 20–22.
- (53) Cihaner, A.; Algi, F. *Adv. Funct. Mater.* **2008**, *18*, 3583–3589.
- (54) Huang, L.-T.; Yen, H.-J.; Chang, C.-W.; Liou, G.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4747–4757.
- (55) Ikeda, T.; Stoddart, J. F. *Sci. Technol. Adv. Mater.* **2008**, *9*, No. 014104.
- (56) Kim, Y.; Dyer, A.; Kim, H.; Reynolds, J.; Graham, S. *Organic Electronics* **2011**, submitted.