Enhanced Contrast Dual Polymer Electrochromic Devices

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The ability to match two complementary polymers constitutes an important step forward in the design of electrochromic devices (ECDs). Here we show that the necessary control over the color, brightness, and environmental stability of an electrochromic window can be achieved through the careful design of anodically coloring polymers. For this purpose, we have constructed ECDs based on dimethyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Me$_2$) as a cathodically coloring layer, along with poly[3,6-bis(2-ethylenedioxythienyl)-*N*-methyl-carbazole] (PBEDOT-NMeCz) and *N*-propane sulfonated poly(3,4-propylenedioxypyrrole) (PProDOP−NPrS) as anodically coloring polymers. Comparison of the results shows that using PProDOP−NPrS as the high band gap polymer has several advantages over the carbazole counterpart. The main benefit is the opening of the transmissivity window throughout the entire visible spectrum by moving the $\pi-\pi^*$ transition of the neutral anodically coloring material into the ultraviolet region. Another advantage of the PProDOP−NPrS based device is the noticeable increase in the optical contrast as evidenced by an increase in the transmittance change of the device ($\Delta\%T$) from 56% to 68%, as measured at 580 nm. These devices exhibit a 60% change in luminance along with half-second switching times for full color change. Moreover, they were found to retain up to 86% of their optical response after 20 000 double potential steps, opening up new directions in optical technology.

Introduction

There are numerous processes possible for the modulation of visible light. Among them are electrochromic techniques that use the reversible change of color and/or optical density obtained by an electrochemical redox process in which the oxidized and the reduced forms have different colors, indices of refraction, or optical densities. These techniques are readily employed in a multitude of applications such as display panels,[1] camouflage materials,[2] variable reflectance mirrors,[3] and variable transmittance windows.[4−6]

Electrochromic devices (ECDs) based on inorganic semiconductors have a long history, and their performance has improved steadily since their creation.[7] When viewed in this context, the recent rapid progress made with organic conducting and electroactive polymers in a variety of fields suggests they may find numerous practical applications in the near term.[8] These materials have made valuable contributions to the emerging fields of ECDs,[4] as well as organic light emitting diodes[9,10] and photovoltaics.[11] In terms of electrochromics, the range of colors now available effectively spans the entire visible spectrum[12] and also extends through the near and mid-infrared regions.[3] This is due to the ability to synthesize a wide variety of polymers with varied color, through modification of the structure of the polymer via monomer functionalization,[13] copolymerization,[14,15] and the use of blends,[16] laminates,[17] and composites.[2,18,19] Device lifetimes have been increased via control of the degradation processes within the polymeric materials (by lowering the occurrence of structural defects during polymerization) and
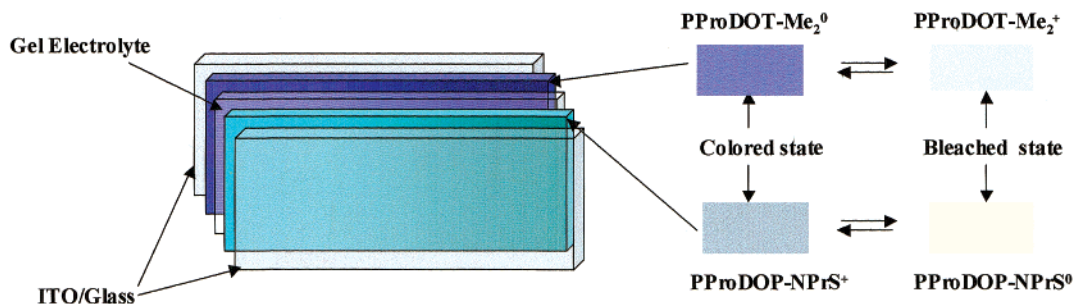
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Scheme 1. Schematic Representation of a Transmissive Type ECD where the Color Representations Shown on the Right Are $L*a*b*$ Determined Color Coordinates

the redox system.[20,21] The polymer based ECDs have achieved relatively fast switching times of a few hundreds of milliseconds for large changes in optical density, because of the highly open morphology of electroactive films, allowing for fast dopant ion transport.[22] Other beneficial properties of polymers are outstanding coloration efficiencies[23] along with their general processability.

The construction of an absorption/transmission type ECD is depicted in Scheme 1. It consists of two thin polymer films deposited on transparent electrodes and separated by an electrolyte. The device construction is carried out with one polymer oxidatively doped while the other is neutral, and both films are simultaneously in either their transmissive or absorptive states. As such, the device is observed as bleached or colored. Application of a voltage neutralizes the doped polymer with concurrent oxidation of the complementary polymer, inducing color formation, or bleaching. The ability to match the number of redox sites in each film enhances the contrast of the device, as the extremes of absorption and transmission can be attained. A cathodically coloring polymer passes from an almost transparent state to a highly colored state upon positive charge neutralization (reduction), whereas an anodically coloring polymer is highly transmissive neutral and absorbs visible light in the oxidatively doped state.

Some of the most promising conducting polymers for use in ECDs are based on poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives, as they exhibit high electrochromic contrasts, low oxidation potentials, and high conductivity, as well as good electrochemical and thermal stability.[13] From the PEDOT derivative palette available in our labs,[12] PProDOT-Me$_2$ stands out as the best cathodically coloring polymer for use in electrochromic devices.[24] We use it in this study as it shows the highest contrast of all polymers we have studied in the visible region (about 78% change in transmittance at 580 nm), and a luminance change[12] of >60% measured by colorimetry. This high contrast at 580 nm corresponds to a wavelength where the human eye is highly sensitive, the polymer switching from a highly transmissive light blue in the doped state

to a dark blue−purple in the neutral state. The color representations shown in Scheme 1 upper right are the 1976 uniform color space $L*a*b*$ determined color coordinates.[25] We have already successfully incorporated PProDOT-Me$_2$ into a variable reflectance ECD showing a remarkably high contrast throughout the visible, NIR, and mid-IR regions of the electromagnetic spectrum. The device allowed for 10 000 deep double potential cycles with only 20% loss in contrast.[3]

Ideally, an anodically coloring polymer is chosen to have a high band gap (E_g) > 3.0 eV (π to $\pi*$ transition onset < 410 nm) with all of the absorption lying in the ultraviolet region of the spectrum. In addition to the required complementary optical properties, proper ECD operation demands a high degree of electrochemical reversibility and compatibility. Our group has designed and synthesized several anodically coloring polymers based on carbazole, biphenyl, and other aromatic units linked via electropolymerizable EDOT moieties.[26,27] Although ECDs incorporating these types of polymers showed outstanding coloration efficiencies, lifetimes, and switching times,[21,22] the band gaps of the anodically coloring polymers were not sufficiently high for the $\pi−\pi*$ absorption to be excluded from the visible region providing a coloration to the transmissive state of the devices. Recently, we reported the synthesis,[28] electropolymerization, and redox switching properties of a new series of conducting polymers based on 3,4-alkylenedioxypyrroles.[29−31] As pyrroles have somewhat elevated LUMO levels relative to thiophene, the band gaps for poly(3,4-ethylenedioxypyrrole) (PEDOP, 2.0 eV) and poly(3,4-propylenedioxypyrrole) (PProDOP, 2.2 eV) are higher than their thiophene counterparts (PEDOT and PProDOT) which have band gaps of 1.6−1.7 eV.

To elevate the band gap of the dioxypyrrole polymers even further, we have prepared a series of N-substituted ProDOPs.[28,32] N-substitution is known to induce a torsional angle between heterocyclic rings along the

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backbone, resulting in a decrease of the π conjugation and therefore an increase in the band gap. In addition to the advantage of this high band gap, these polymers preserve the electron rich character of the PXDOP family, allowing electrosynthesis and switching under mild conditions. Polymerization is forced through the 2 and 5 positions as desired giving rise to a material with few structural defects and, consequently, better electrochemical cyclability when compared to the parent polypyrrole.[31] By judicious selection of the N-alkyl substituent, we have prepared an N-propane sulfonated PProDOP (PProDOP−NPrS) where the onset of the $\pi-\pi^*$ transition is located at the boundary of the visible and ultraviolet regions of the spectrum (E_g = 3.0 eV). As such, the electronic absorption is transferred to the UV, and the polymer is colorless in the neutral state. PProDOP−NPrS switches from a gray−green state to an almost clear neutral state, as seen in Scheme 1, lower right. Moreover, the presence of a sulfonate group at the end of the propyl chain offers the possibility of self-doping along with water solubility of the resulting polymer. As a result, PProDOP−NPrS exhibits a fast and regular growth even in the absence of supporting electrolyte.

Results and Discussion

Here, we report our research efforts focused on attaining extremely high contrast in dual polymer ECDs by matching the anodically and cathodically properties in order to obtain a color neutral, highly transmissive window in one state, which shows low absorption throughout the entire visible region. Upon switching a small bias voltage (ca. 1.0 V), the window is converted to a relatively colored dark state. Figure 1 demonstrates this concept by superimposing the UV−visible spectra of the individual polymers in their doped and neutral states. Figure 1A represents the absorptive state where PProDOP−NPrS is in the oxidized form, and PProDOT-Me$_2$ is in the neutral state. The summation of the two absorption spectra represents the most probable behavior of the colored state of a device based on these two polymers. There are several factors that combine to attain a very saturated color and broadband absorbance window. First, neutral PProDOT-Me$_2$ has its absorption in the middle of the visible region (λ_{max} = 580 nm) where the human eye is highly sensitive. In addition, the vibrational splitting of the HOMO−LUMO transition broadens the absorption peak over a larger area of the visible spectrum. The absorption of the oxidatively doped PProDOP−NPrS begins at 500 nm, and its absorbance increases into the NIR region where the contribution from neutral PProDOT-Me$_2$ is small. The bleached state of the polymer films and device is represented in Figure 1B. The sum of the neutral PProDOP−NPrS and doped PProDOT-Me$_2$ spectra provide a high contrast with the colored state throughout the entire visible region, generating a highly transmissive device.

Figure 2 shows the transmittance spectra and photographs of devices using PProDOT-Me$_2$ as the cathodically coloring polymer and PBEDOT-NMeCz (**A**) and PProDOP−NPrS (**B**) as the anodically coloring layers with the devices in the two extreme (colored and bleached) states. Matching the number of redox sites
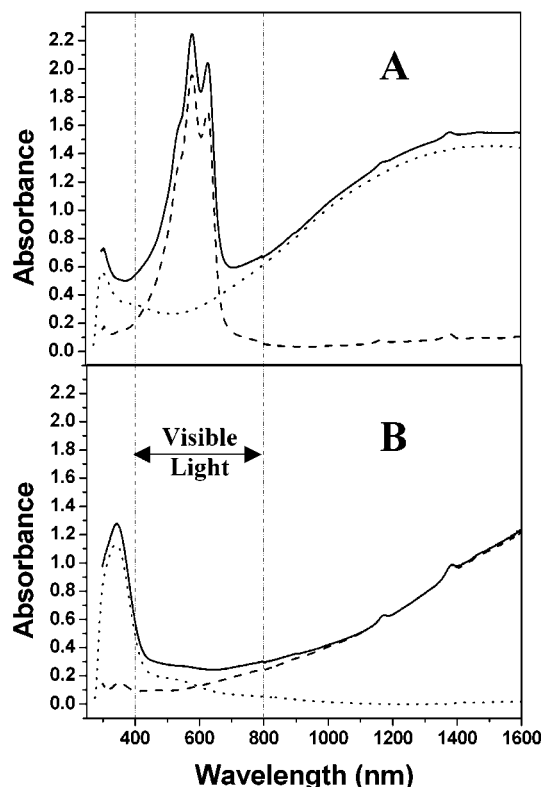

Figure 1. Superimposition of the UV−vis−NIR spectra of the individual polymer films deposited on ITO/glass substrates. Figure 1A represents the polymers' absorptive states where PProDOP−NPrS is in the oxidized form (dot line) and PProDOT-Me$_2$ is in the neutral form (dashed line). The summation of the two absorption spectra (solid line) represents the most probable behavior of the colored state of a device based on these two polymers. Figure 1B represents the bleached state of the polymer films. The sum of the neutral PProDOP−NPrS (dot line) and doped PProDOT-Me$_2$ (dashed line) spectra provide a high contrast with the colored state throughout the entire visible region, generating a highly transmissive device (solid line). For clarification purposes, the visible region of the spectrum (400−800 nm) is marked with dashed vertical lines.

in each film was attained by matching polymer layer thicknesses. In this study, all of the polymer films are ca. 200 nm thick, as measured by profilometry. Both devices switch between the two forms when a bias voltage of ±1.0−1.5 V is applied. When voltages are applied continuously between +1 and −1 V, the devices change from colored to transmissive and the spectra evolve from one extreme to the other. Comparison of the results shows that using PProDOP−NPrS as the high band gap polymer has several advantages over the carbazole counterpart. The main benefit is the opening of the transmissivity window throughout the entire visible spectrum by moving the $\pi-\pi^*$ transition into the ultraviolet region. The cutoff of the PBEDOT-NMeCz is evident at ca. 500 nm. Another advantage of the PProDOP−NPrS based device (**B**) is the noticeable increase in the optical contrast as evidenced by an increase in the transmittance change of the device ($\Delta\%T$) from 56% to 68% measured at 580 nm. Furthermore, although doped PBEDOT-NMeCz is blue and its charge carrier absorption is at the same energy as the $\pi-\pi^*$ transition of the low gap PProDOT-Me$_2$ absorption, PProDOP−NPrS is gray−green in the oxidized state, thus providing some extra blocking of the transmission of the colored device in the 400−500 nm region.
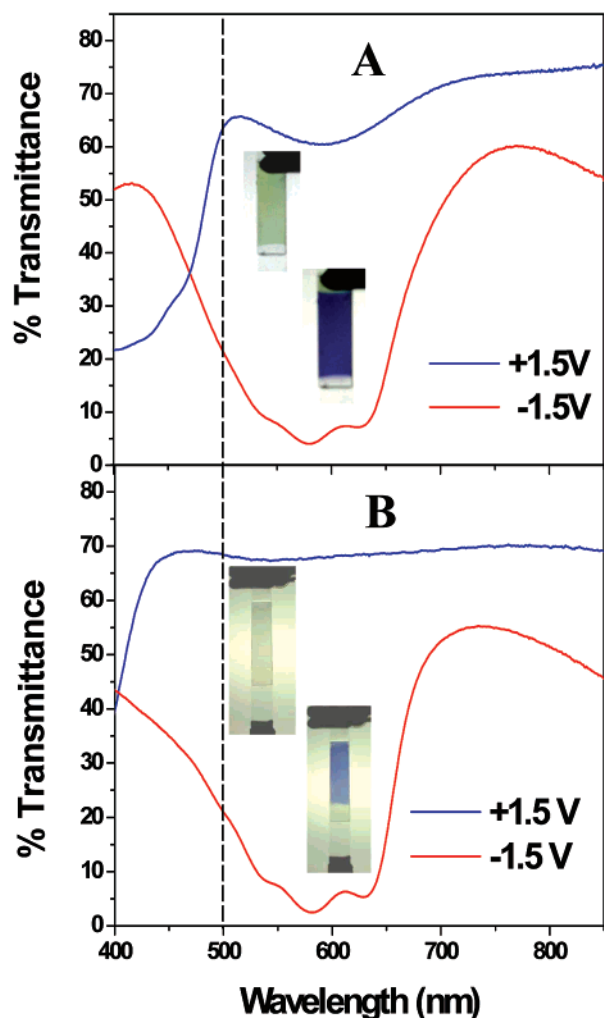
Figure 2. Transmittance spectra and photographs of devices using PProDOT-Me$_2$ as the cathodically coloring polymer and PBEDOT-NMeCz (A) and PProDOP−NPrS (B) as the anodically coloring layers with the devices in the two extreme (colored and bleached) states. The dashed vertical line represents the onset of the cutoff of the neutral PBEDOT-NMeCz.

One of the most important characteristics of ECDs is the response time needed to perform a switch from transmissive to colored and vice versa. To analyze the switching characteristics of these windows, the variation in monochromatic light at the wavelength of maximum contrast was monitored during repeated redox stepping experiments. For a comparison, we monitored the change in transmittance of a single PProDOT-Me$_2$ film of the same thickness (about 200 nm) as the films used in the devices. As seen in Figure 3A, both devices switch quite rapidly. The PProDOT-Me$_2$ film alone can be effectively switched in about 0.5 s to attain 95% of its total transmission change (%ΔT = 76%). Although device A switches in about 500 ms, device B has a somewhat larger dynamic range with a total % transmission change in 600 ms. However, it is remarkable that by adding the PProDOP−NPrS layer device B loses only 10% in overall contrast compared to a single PProDOT-Me$_2$ film.

Recently, colorimetric analysis[12] has been used to investigate the properties of electrochromic and light-emitting polymers. Both luminance and x−y chromaticity diagrams provide valuable information for understanding changes in the devices color and/or brightness.
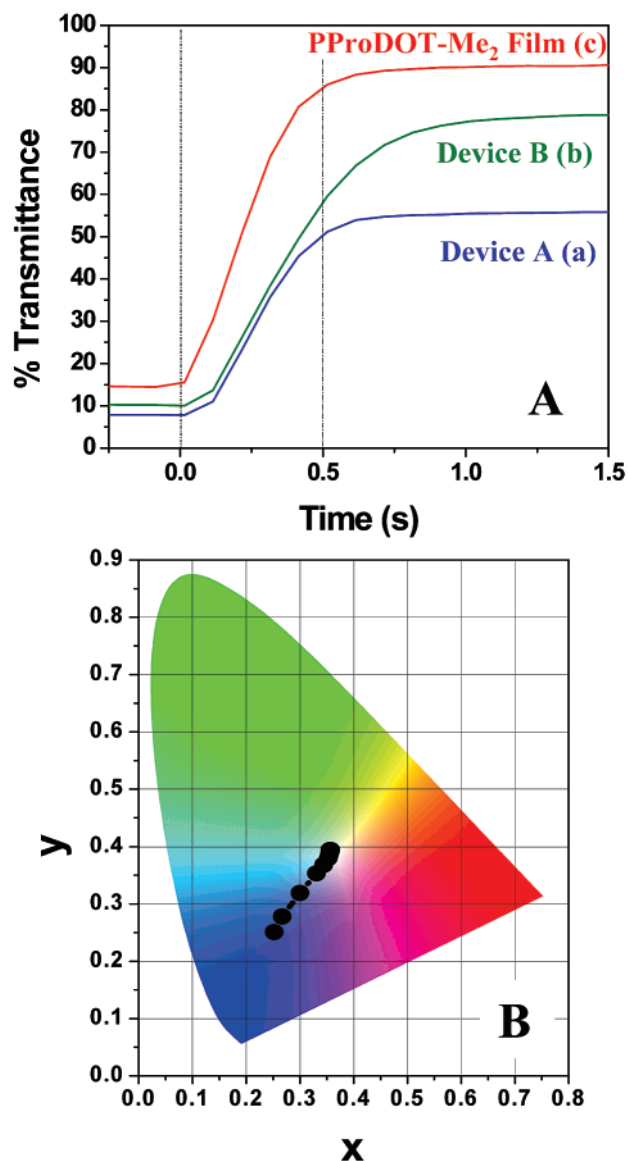

Figure 3. (A) Transmittance as a function of switching time of the (a) PProDOT-Me$_2$/ PBEDOT-NMeCz device, (b) PPro-DOT-Me$_2$/PProDOP−NPrS device, and (c) PProDOT-Me$_2$ film. (B) Representation of the hue and saturation x−y track for the device as the applied potential changes from −2.5 to +1.5 V.

For example, the potential dependence of the relative luminance offers a perspective on the transmissivity of a material as it relates the human eye perception of transmittance over the entire visible spectrum as a function of doping on a single curve. Figure 3B shows the hue and saturation x−y track for device B as the applied potential is changed from −2.5 to +1.5 V, which corresponds to the oxidative doping track of PProDOT-Me$_2$. A straight line spans from the dark blue area in color space to a highly transmissive (near white point) pale blue−green color. The potential dependence of the relative luminance (Figure 4) shows that, in the bleached state, the window exhibits a luminance of 65% through the positive voltage values. A voltage of −0.5 V is needed to induce a decrease in luminance; dimming of the device luminance continues to increase until a potential of −2 V is attained. The overall luminance change, that is in essence the optical density change perceived by the human eye, is 55%.
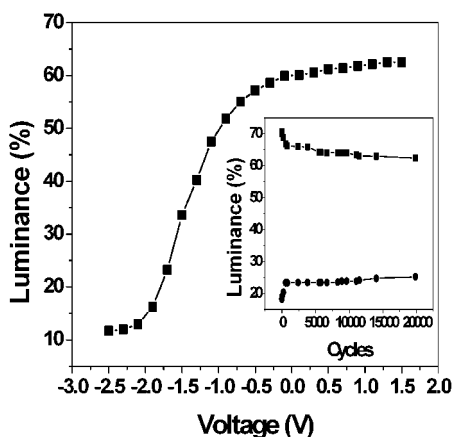
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Figure 4. Luminance analysis of PProDOT-Me₂/PProDOP−NPrS device. The lower right inset shows the lifetime of the PProDOT-Me₂/PProDOP−NPrS device to multiple electrochromic switches. The upper trace (■) shows the decrease in the luminance of the device in the bleached state with the number of cycles performed, whereas the lower trace (●) is the fading of the dark state during continuous switching.

The stability of the bleached and/or colored states toward multiple redox switches often limits the utility of electrochromic materials in ECD applications. Main reasons for device failure are different electrochemical windows and/or environmental requirements of the complementary materials. If the two EC materials possess different electrochemical windows for operation, then the applied voltage needed for attaining 100% of the optical contrast increases. Therefore, longer lifetimes are expected for devices operating at low voltages because high-applied potentials are detrimental to the electrochromic films, to the electrolyte, and even to the ITO layer. The oxidation process of the anodic material should coincide with the reduction process of the cathodic EC material in order to properly maintain charge balance within the ECD.

We employed colorimetry by monitoring the luminance change to investigate the long-term stability for device B to multiple deep switches (Figure 4, inset). This study was carried out by continuously stepping the voltage of the device between −1 and +1 V with a 30 s delay at each potential allowing a full color change and hold period. During this time, the luminance was monitored over a period of 7 days. We noticed that the device loses 10% of its contrast during the first 500 cycles. After this conditioning period, the degradation proceeds remarkably slowly, and the device loses only 4% of its luminance contrast over a period of 20 000 double potential cycles. As the devices are sealed to ambient exposure, significantly longer lifetimes are realized.

Conclusions

The dual polymer ECDs reported herein possess the ability to operate at low applied voltages (±1.0V) with both films being compatible in the same electrochemical environment. This greatly increases their lifetime to 86% retention of their initial color (96% retention after break-in) after 20 000 cycles. Most importantly, the newly discovered PProDOP−NPrS has the ability to switch between a colorless neutral state to a doped gray−green state, possessing the rare property of being a truly anodically coloring polymer with easily accessible

redox switching potentials. Furthermore, doped PPro-DOP−NPrS broadens the absorption peak of the dark state ECD in both the 400−500 and 700−800 nm regions of the visible spectrum, where the contributions from the π−π* transition of the PProDOT-Me₂ film are small. The devices based on PProDOP−NPrS and PProDOT-Me₂ complementary polymers exhibit an optical contrast of up to 70% at λ_{max} as well as an overall luminance change of 53%. They switch from a transparent state to a very dark, almost opaque state in less than 1 s, potentially making them useful polymer displays. All of the above characteristics show that the use of carefully designed complementary polymers is a promising route for achieving the necessary control over the color, brightness, and environmental stability of an electrochromic window.

Experimental Section

Chemicals. ACN and PC were purchased from Aldrich in Sure Seal bottles under Ar. Although PC was used as received, ACN was distilled over calcium hydride prior to use. The monomers were obtained as follows: ProDOT-Me₂,[24] PBEDOT-NMeCz,[33] and ProDOP−NPrS[28] were synthesized according to methodologies previously reported. LiClO₄ and Li[N(CF₃SO₂)₂] were purchased from Aldrich and 3M, respectively, and used without further purification.

Polymer Deposition. Electrochemical deposition of the polymer layers was carried out using an EG&G model 273A potentiostat/galvanostat. A three electrode cell with Ag/Ag⁺ as the reference, ITO/glass as the working, and a platinum flag as the counter electrode was used for electrosynthesizing the polymer films. The films were prepared from 10 mM monomer in lithium perchlorate/PC solutions. We applied 0.7 V for ProDOP−NPrS polymerization, 0.5 V for BEDOT-NMeCz, and 1.1 V for ProDOT-Me₂ (all potentials are reported versus a Ag/Ag⁺ reference). The film thicknesses were measured utilizing a Dektak Sloan 3030 profilometer.

Gel Electrolyte Preparation. A gel electrolyte based on PMMA and Li[N(CF₃SO₃)₂] was plasticized by PC to form a highly transparent and conductive gel. To allow an easy mixing of the gel components, we included ACN as a high vapor pressure solvent. The composition of the casting solution by weight ratio of ACN:PC:PMMA:Li[N(CF₃SO₃)₂] was 70:20:7:3.

Device Assembly and Characterization. The CP coated ITOs were rinsed with freshly distilled acetonitrile. The films were then coated with gel casting solution until the entire polymer surface was covered with a uniform and thin layer of electrolyte. The selected cathodically and anodically coloring electrodes were then applied to one another and allowed to dry for 24 h. The gel electrolyte formed a seal around the edges, with the devices becoming self-encapsulated. The devices' spectroelectrochemistry was carried out using a Varian Cary 5 E spectrophotometer. The polymers' doping level was adjusted in a specially designed three-electrode spectroelectrochemical cell.

Colorimetric Studies. Colorimetry results were obtained by the use of a Minolta CS-100 Chroma Meter. The sample was illuminated from behind by a D50 (5000K) light source in a light booth specially designed to exclude external light. A background measurement was taken using a blank device containing two ITO glasses held together by the gel electrolyte.

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