

Broadly Absorbing Black to Transmissive Switching Electrochromic Polymers

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Non-emissive electrochromic devices (ECDs), which can be operated under a wide range of viewing and lighting conditions, are especially attractive in applications that include smart windows, displays, electronic paper and mirrors.^[1–4] Consequently, the processability, flexibility, high optical contrast, rapid redox switching and long-term stability of easily oxidized conjugated polymers has made them desired materials for various reflective/transmissive ECDs.^[5–7] Although many polymeric electrochromes which are colored (red and orange,^[8] green,^[9–11] magenta/purple,^[12] and blue^[13–17]) in the neutral state and highly transmissive in the oxidized state have been investigated, there are only two black-to-transmissive electrochromic polymers (ECPs) reported to date.^[18,19] This is due to the complexity in inducing a polymer absorption spectrum which absorbs evenly over the entire visible spectrum (400–750 nm) in the fully neutralized state, while effectively bleaching out in the same region in the fully oxidized state.

In order to create conjugated polymers with neutral state colors of blue, green or black, the materials' optically estimated band gap must be lower than 1.75 eV. The "donor-acceptor" (DA)^[20–22] approach has successfully been utilized to achieve these low-gap polymers for organic photovoltaics,^[23–26] field-effect transistors^[27,28] and light emitting diodes.^[29] DA type polymers generally show two distinct optical absorption bands, which can be modulated as a function of the composition of donor and acceptor moieties in the main chain.^[30–32] The tuning of the dual-band absorption character of DA type polymers provides an elegant method of modifying spectral characteristics to achieve desired colors.

In recent work, we reported the synthesis and characterization of the first black-to-transmissive switching polymeric electrochrome based on the donor-acceptor approach.^[18] We showed that by variation of the relative contribution of electron-rich and -poor moieties in the polymer backbone, the two-band absorption in the visible spectrum could be controlled. In addition, using a particular feed ratio of two different monomers, the discrete absorption bands merged into a broad absorption across

the entire visible spectrum. The spray-cast polymer thin film exhibited a deep black neutral state and attained a highly transmissive state when fully oxidized. Due to the synthetic complexity of the polymer, which involved the synthesis and chromatographic separation of DAD trimers, and which may limit reproducible large-scale production of the material, we desired to develop a method that would lead to polymer batches with highly reproducible absorption spectra and an efficient, scalable and consistent polymerization process.

As illustrated by **Figure 1a**, we demonstrate a facile synthetic approach to access black-to-transmissive electrochromic polymers via a random transition-metal mediated coupling polymerization. In the specific instance reported here, we use a Stille polymerization; however the method could be applied to many other transition-metal mediated reactions that include Suzuki, Negishi, and Kumada couplings. Under the most common Stille polymerization conditions, two monomers (typically an aryl distannane and an aryl dihalide) are cross-coupled using palladium catalysis to produce polymers with pre-determined Ar-Ar' couplings.^[33–35] In this approach, we desired to incorporate a random mixture of donor and acceptor heterocycles in order to achieve a black polymer by utilizing more than two monomeric species in the polymerizations.^[36,37] In order to simulate the ratio of electron-rich to electron-poor heterocycles determined in our previous work, we chose to randomly polymerize both 2,5-dibromo- and 2,5-tributylstannyl-2-ethylhexyloxy-substituted 3,4-propylenedioxythiophene (ProDOT-(CH₂OEtHx)₂) with 4,7-dibromo-2,1,3-benzothiadiazole (BTD) in different feed ratios. In an optimization of the feed ratio, five random broadly absorbing copolymers (**ECP-1** through **ECP-5**) were produced, with number average molecular weights (M_n) around 10 to 15 kDa and polydispersities ranging from 1.3 to 1.6 after fractionation (see Supporting Information, Table S1).

The UV-visible absorption spectra of the polymers in chloroform are shown in **Figure 1b**. A broad spectral absorption is evident ranging from approximately 400 nm to greater than 700 nm for each polymer. Unlike the spectra of typical donor-acceptor polymers, which generally have two distinct absorption bands, the spectra of polymers **ECP-1** to **ECP-5** show a "merging" of the short- and long-wavelength optical transitions, and no obvious peak to peak window is observed. As expected, **ECP-1** exhibits the lowest intensity of the short-wavelength absorption at 461 nm due to its relatively low concentration of electron-rich moiety. Considering the reduced absorption of blue and green light (400–580 nm), as well as an absence of far-red light absorption from 700 to 750 nm, it is reasonable that the solution of **ECP-1** gives a midnight blue color. By increasing the relative amount of ProDOT-(CH₂OEtHx)₂ repeat unit, the

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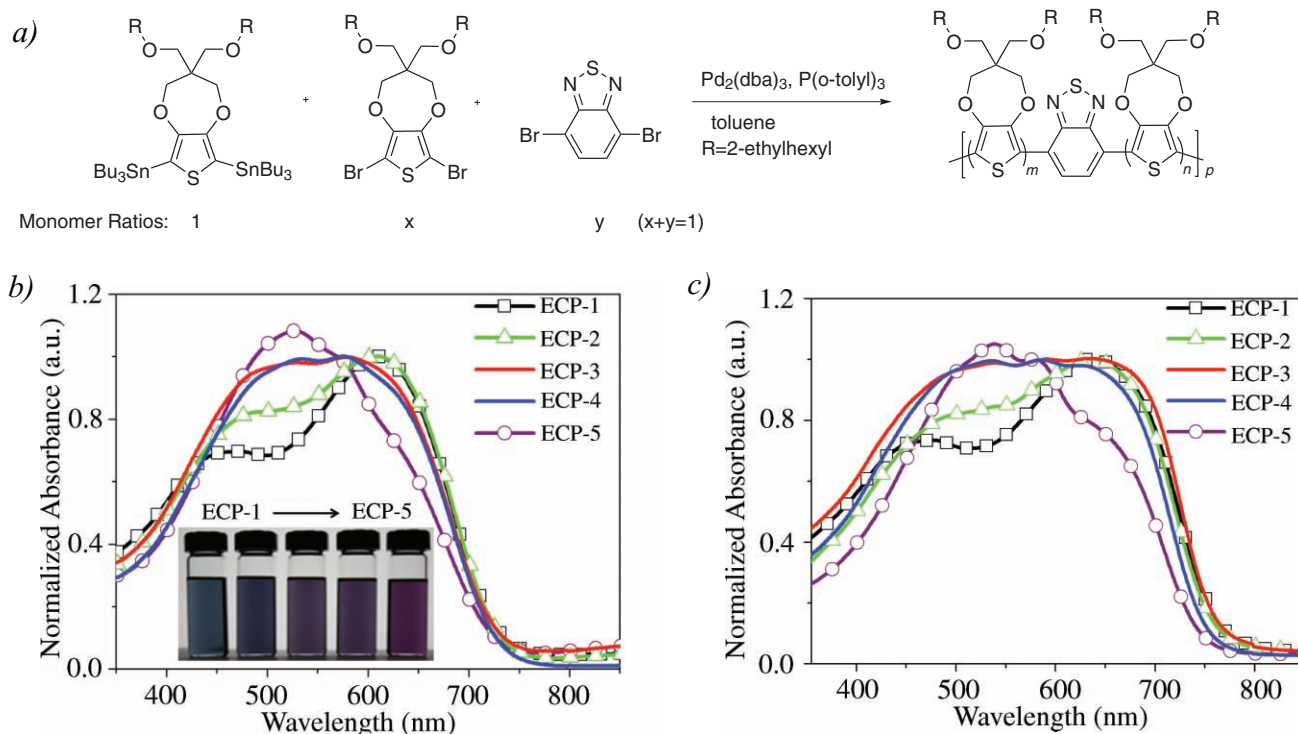


Figure 1. a) Reaction scheme for the Stille polymerization of three monomers. b) Solution absorption of Polymer **ECP-1** (monomers ratio: $x = 0.6$, $y = 0.4$), **ECP-2** ($x = 0.7$, $y = 0.3$), **ECP-3** ($x = 0.75$, $y = 0.25$), **ECP-4** ($x = 0.76$, $y = 0.24$) and **ECP-5** ($x = 0.8$, $y = 0.2$) in chloroform. The inset shows the various colors obtained across the polymer series. c) Normalized film absorption of Polymer **ECP-1**, **ECP-2**, **ECP-3**, **ECP-4** and **ECP-5** (the films were spray-cast onto ITO-coated glass from toluene (2 mg mL^{-1})).

difference in intensity between the two absorption bands is reduced. At a specific point where the donor/acceptor ratio is approximately 7 to 1, the intensities of the two bands are balanced, and homogenous absorptions across most of the visible spectrum (450–650 nm) are observed for **ECP-3** and **ECP-4**. Not surprisingly, solutions of **ECP-3** and **ECP-4** show a similar dark-purple-black color due to the lack of absorption in the far blue and red regions. Accordingly, the absorption of **ECP-5** shows a higher intensity of the high energy transition (530 nm) than its low energy transition (572 nm) with a further increase of the donor concentration, and the solution of **ECP-5** exhibits a bright purple color due to the increased reflection/transmission of red light.

Two additional syntheses of polymer **ECP-3** were undertaken to demonstrate successful repeatability. The generated polymers **ECP-3-s1** and **ECP-3-s2** are consistent with **ECP-3** in terms of molecular weight (M_n), PDI and solution absorption (see Supporting Information, Table S1 and Figure S1). As expected, by controlling the feed ratio of the monomers, we were able to effectively manipulate the absorption pattern of the polymers.

Thin films of each polymer were then spray-cast onto indium tin oxide (ITO) coated glass slides from toluene solution (2 mg mL^{-1}). The visible absorption spectra of the films shown in Figure 1c exhibit a broadening of the long wavelength absorption with little to no change at the higher energy end of

the spectra in the solid state compared to solutions for all five polymers. The significant extension of absorption into the far red region is important as it leads to a more pure black color of the films. As determined from the onset of their neutral-state lower-energy optical transition, the polymers give a relatively low band gap ranging from 1.6–1.7 eV.

Figure 2a shows the full spectroelectrochemical behavior of an **ECP-3** film. The film was redox cycled to a stable and reproducible switch prior to the analysis, and then electrochemically oxidized from -0.25 to $+0.35 \text{ V vs. Fc/Fc}^+$ (in 25 mV steps). Upon oxidation of the polymer, the broad absorption in the visible region is depleted, and a polaronic transition in the near-IR (800–1200 nm) arises, and then falls as a bipolaronic transition further in the NIR appears. When fully oxidized, the generated bipolaronic absorption peaks beyond 1600 nm, which allows effective bleaching of the visible absorption, and a remarkably high level of transmissivity to the human eye. In order to further accentuate the optical changes that occur upon oxidation, the electrochromic response is shown in terms of transmissivity across just the visible region in Figure 2b from 350 nm to 750 nm. For a film of **ECP-3** in its neutral state, a nearly flat transmittance profile at 20% from 450 nm to 700 nm is observed. In contrast, when the film is fully oxidized, the transmittance increases to above 60% through most of the visible region. The electrochromic contrast (as percent transmittance change, $\Delta\%T$) is as high as

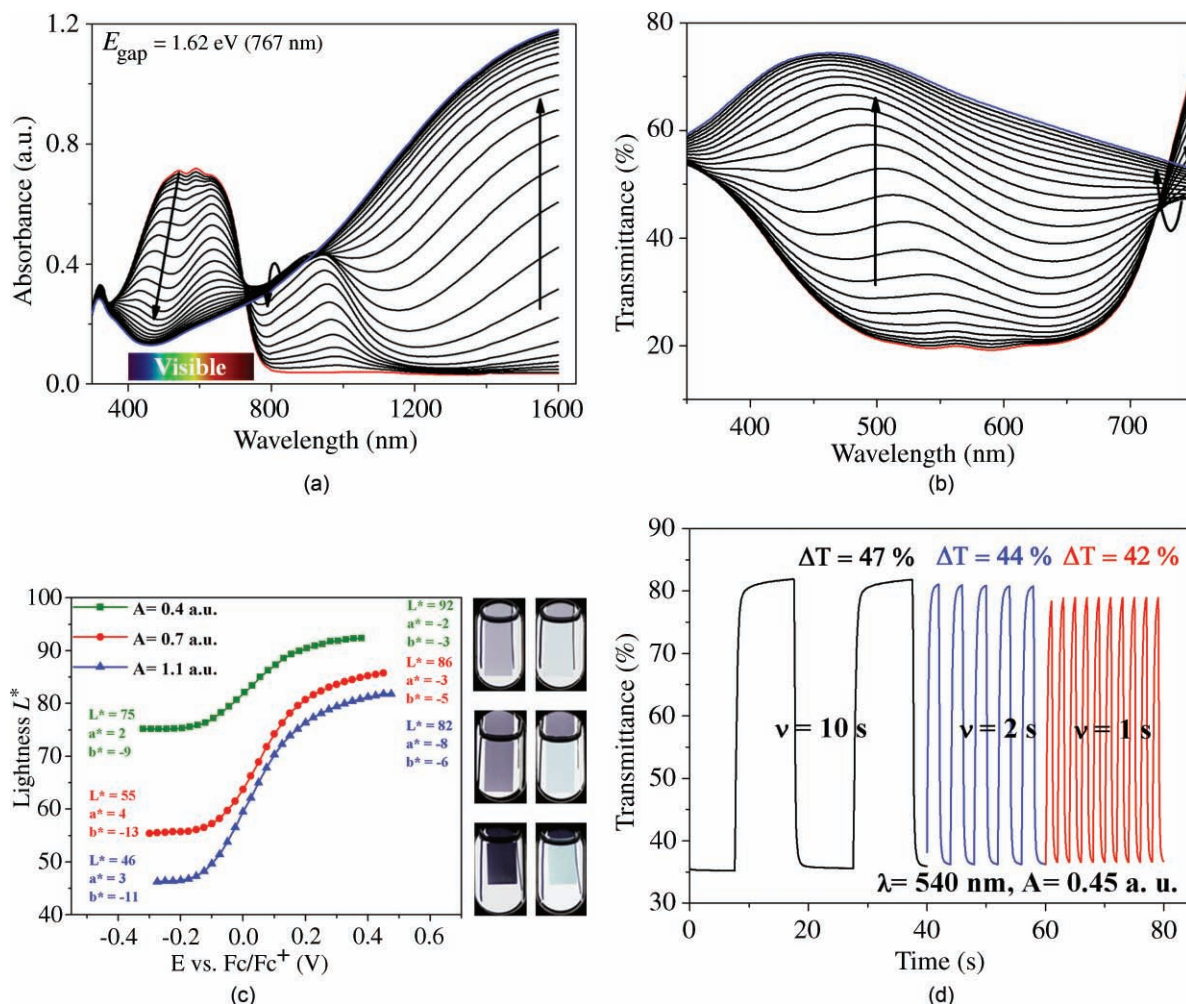


Figure 2. a) Spectroelectrochemistry of **ECP-3**. The films were spray-cast onto ITO-coated glass from toluene (2 mg mL^{-1}). Electrochemical oxidation of the films was carried out in 0.1 M lithium bistrifluoromethanesulfonamide (LiBTf)/propylene carbonate (PC) solution, supporting electrolyte using a silver wire as a quasi reference electrode (calibrated against Fc/Fc^+), and a platinum wire as the counter electrode. The applied potential was increased in 25 mV steps from -0.25 to $+0.35 \text{ V vs. } \text{Fc}/\text{Fc}^+$. b) Electrochromic response in terms of transmissivity in the visible region (replotted from Figure 2a). c) Lightness (L^*) as a function of applied potential for spray-coated **ECP-3**. $L^*a^*b^*$ values of fully neutral and oxidized states are reported for the films. Photographs are of the fully neutral (left) and fully oxidized films (right). d) Square-wave potential-step chronoabsorptometry of **ECP-3** spray-coated on ITO (monitored at 540 nm , -0.72 to $+0.48 \text{ V vs. } \text{Fc}/\text{Fc}^+$ in 0.1 M LiBTf/PC electrolyte solution). The step times (10 s , 2 s and 1 s) are indicated on the figure.

48% at 555 nm , the wavelength at which the human eye has greatest sensitivity.

To evaluate the color changes of the ECPs occurring on electrochemical switching (on the basis of the “Commission Internationale de l’Eclairage” 1976 $L^*a^*b^*$ color standards), three **ECP-3** films with varying thicknesses were subjected to colorimetric analysis. Figure 2c shows the determined CIE 1976 L^* values as a function of applied voltage that gives an indication of relative brightness of the film as it is oxidized while illuminated from behind (transmission mode) with a standard D50 simulated daytime light source. In their neutral state, the polymer films exhibit L^* values from 46 for the thickest film to 75 for the thinnest film. Importantly, the film with absorption maximum of 1.1 a.u. displays a deep black color with a^* and b^* values as low as 3 and -11 . This observation is consistent

with the visible absorption spectra of **ECP-3** thin film as a small amount of red and slightly more blue light is transmitted by the polymer. In comparison, the fully oxidized polymer films exhibit high L^* values from 82 to 92 with smaller a^* and b^* values, which demonstrates that this polymer is able to reach a highly transmissive near colorless state as defined by the $L^*a^*b^*$ color coordinates.

Given that the speed at which electrochromic materials change color states is important in display-type devices, the film switching rate was examined by monitoring the transmittance change at a single wavelength (EC contrast, $\Delta\%T$) as a function of time by applying square-wave potential steps for periods of 10, 2 and 1 s. As shown in Figure 2d, a transmittance change (monitored at 540 nm) as high as 47% is recorded at the longer switch time (10 s), and decreasing the switch time to

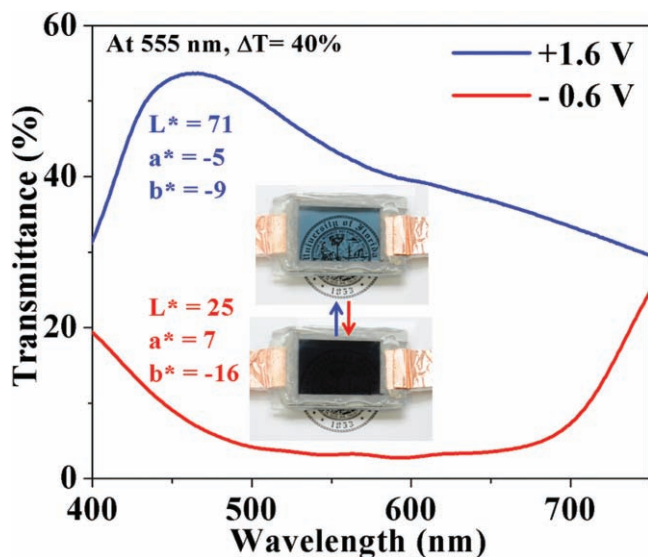


Figure 3. Transmittance spectra of ECD in extreme states of highly absorptive (at an applied cell voltage of -0.6 V) and highly transmissive (at an applied cell voltage of $+1.6$ V). The insets show photographs of the same device in both states.

1 s, is reduced to 42%, only a 5% loss. As stability to repeated redox switching is also essential to the practical utilization of these materials in EC devices, the EC contrast (ΔT at 540 nm) of a film was monitored while repeated square-wave potential steps of 1.5 s (complete cycle is 3 s, switching between -0.72 to $+0.48$ V vs. Fc/Fc^+) for 18,000 cycles (Figure S2) were applied. The polymer exhibits a continuous switching stability with only a decrease of 8% in electrochromic contrast over this time period.

To further reinforce the utility of these polymers, we have demonstrated black-to-transmissive switching in an absorptive/transmissive window-type electrochromic device. Using the device structure as detailed in Figure S3, the polymer ECP-3 was utilized as the actively switching material at the working electrode, and a minimally color-changing polymer (N-alkyl substituted poly(3,4-propylenedioxyppyrole)), which is similar to that previously described by our group,^[38] was used as the charge-balancing material at the counter electrode. As shown in Figure 3, the transmittance spectra of the device in both the dark state and transmissive state were measured across the visible region from 400 to 750 nm. Higher transmittance in the blue region is observed when the polymer is in the oxidized state giving a highly transmissive light blue color. Conversely, when the polymer is neutralized at a device cell potential of -0.6 V, the transmittance decreases to a near featureless spectral profile with the device having a contrast of $\sim 40\%$ at 555 nm. Additionally, an absorptive/reflective display-type device was constructed utilizing polymer ECP-3 as the active electrochrome as detailed in the Supporting Information.

In conclusion, precise control of the absorption spectra of conjugated polymers was achieved by simply varying monomer feed ratios in a random Stille polymerization. This approach produced black-to-transmissive polymer electrochromes with the most broad and uniform visible absorption that have been

reported to date. In addition, the random Stille polymerization was shown to be highly repeatable between different runs. The resulting polymers show a high optical contrast, rapid redox switching and long-term redox stability and have been incorporated into both window-type and display-type electrochromic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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