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Polythieno[3,4-*b*]thiophene as an Optically Transparent Ion-Storage Layer

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Ion storage layers have been employed in the construction of electrochromic devices to enhance device lifetimes through balanced ion shuttling. This has led to a search for a material which has a high charge capacity as well as optical transparency. Poly(thieno[3,4-*b*]thiophene) (PT34bT) exhibits high transparency in the visible region in both its neutral and oxidized states, in addition to having a high charge capacity, making it an ideal candidate for an ion storage layer. Herein we report devices fabricated by electrodeposition of several common chromophores, such as PEDOT, PDiBz-ProDOT, and PProDOT-Me$_2$. Devices were made with and without a balanced layer of PT34bT on the counter electrode and were probed for coloration and contrast. It was found that the addition of the ion storage layer did not alter the color of any of the devices and resulted in a minimal, predicted loss of contrast corresponding to the thickness of the ion storage layer.

Introduction

The switching of conjugated polymers between an insulating and a conducting state is usually accompanied by a change in their absorption/transmittance and ion diffusion, forming the basis of their applications in electrochromics. In general, switching of conjugated polymers to their various oxidation states can also lead to multiple color transitions owing to their broad spectra.[1] Both anodically and cathodically coloring conjugated polymers that switch between a colored state and a transmissive, colorless state are well-known.[2−5] Examples of green to colorless and black to colorless materials have been demonstrated, as well as various IR attenuation devices.[6−10] All of these electrochromic (EC) cells are basically redox cells; that is, an oxidation process in one of the electrodes must be compensated by a reduction in the auxiliary electrode. Thus, a charge compensating layer on the second, auxiliary electrode is indispensable for prolonging the lifetime of the device. A dual polymer approach using an anodically coloring polymer and a cathodically coloring polymer has been demonstrated earlier.[11] In these devices, the anodically and cathodically coloring polymers are complementarily coloring in nature and hence have a synergistic effect in the bleached and colored states. The most commonly used anodically coloring polymers, which are bleached in their neutral state and colored in their oxidized state, are high band gap polymers. For electrochromic applications, the $\lambda_{\max}$ of the neutral high band gap polymers is expected to lay completely within the UV region; in most cases the low energy absorption of the neutral polymer tails into the visible region yielding a yellow color in the bleached state. Yellow is known to distort the perception of color by the human eye, which would be undesirable for applications such as windows or sunglasses. This can be detrimental for some applications, including variable transmittance smart windows and displays. Thus, any ion storage layer which presents any yellowing effects is undesirable. Dual polymer complementary coloring electrochromic windows are effective in variable transmission devices since they synergistically bleach. However, for full color polymeric displays, there is a strong need for one of the conjugated polymers not to exhibit any coloring effect in the visible region in any of the oxidation states. In essence, the second polymer must act as an ion-storage layer alone.

Reynolds and co-workers reported that the use of PProDOP-NPrS (Figure 1), a high band gap polymer

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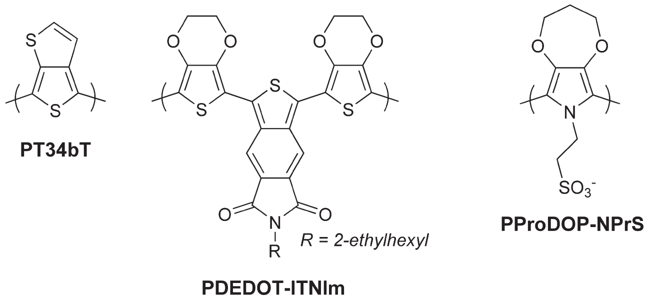

Figure 1. Chemical structures of various ion storage layers, with abbreviations.

with reduced low energy absorption tail in the visible region, can partially eliminate the yellow coloration.[12] This polymer was shown to exhibit a drastic shift in the $\lambda_{\max}$ going from the UV region in the neutral state to the NIR in the oxidized state. Thus, it exhibits very little absorbance throughout the visible region in either of the oxidation states, acting as a neutral density filter. Reported values of contrast losses for the use of this material were on the order of 10%. Wudl and co-workers have suggested the use of a very low band gap conjugated polymer based on 1,3-bis(2′-[3′,4′-ethylenedioxy]thienyl)-benzo[*c*]thiophene-*N*-2″-ethylhexyl-4,5-dicarboximide (DEDOT-ITNIm, Figure 1), as the ion-storage layer in dual polymer electrochromics, although no examples of these have been reported.[13]

Herein, we demonstrate the use of poly(thieno[3,4-*b*]-thiophene) (PT34bT, Figure 1), a low band gap polymer (E_g = 0.85 eV), as the ion-storage layer for a dual polymer electrochromic window. Electrochemically synthesized poly(thieno[3,4-*b*]thiophene) has earlier been reported to be highly transmissive and colorless in the oxidized state and a transmissive sky blue in the neutral state.[14] PT34bT in the neutral state does not exhibit peaks within the visible region, like poly(DEDOT-ITNIm), and hence will not significantly contribute to any coloration effects. Therefore, from an optical point of view, polymers such as PT34bT will be more useful as ion-storage layers. We have also reported a higher doping level for poly(thieno-[3,4-*b*]thiophene) compared to that of poly(3,4-ethylene-dioxythiophene) (PEDOT).[15] The doping ratio remains high when compared to other electrochromic polymers, such as poly(3,4-propylenedioxythiophene) (PProDOT) and its derivatives. These two properties, namely, optical transmissivity and higher charge capacity, are essential in making PT34bT a good candidate for an ion-storage layer in EC windows. Solid-state electrochromic devices were constructed and were comprised of PDiBz-ProDOT, PProDOT-Me_2, and PEDOT (Figure 2) each with PT34bT. These windows were characterized using electrochemical and optical techniques. A maximization of contrast for each of the four polymers was carried out with respect to film thickness and charge per unit area. Furthermore, the color transitions of the single polymers as well as the dual polymer systems are compared using 1976 CIE color space plots, and it was found that PT34bT did not alter the color of any of these devices.

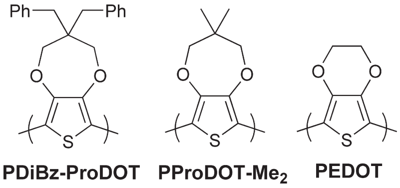

Figure 2. Chemical structures of various electrochromic polymers, with abbreviations.

Experimental Section

Materials. DiBz-ProDOT was a generous gift from Prof. Anil Kumar. 3,4-Dihydro-3,3-dimethyl-2*H*-thieno[3,4-*b*][1,4]dioxepine or 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me_2) was synthesized using a transetherification ring closure starting with commercially available 3,4-dimethoxythiophene (Organic Electronics Chemicals) and 2,2-dimethylpropane-1,3-diol (Sigma-Aldrich) according to the literature procedure.[16] EDOT was purchased from Sigma-Aldrich and distilled before use. Thieno[3,4-*b*]thiophene was prepared via a literature procedure.[13] Acetonitrile (Fisher Scientific) was freshly distilled over calcium hydride (ACROS). Lithium trifluoromethanesulfonate (LITRIF) was purchased from Aldrich and used as received. One sided indium doped tin oxide (ITO) coated SiO_2 passivated unpolished float glass with a nominal resistance of 8−12 Ω purchased from Delta Technologies Inc. was used as received.

Instrumentation. A CHI660A potentiostat was used for all the electrochemical polymerization and characterizations. A Perkin-Elmer UV Lambda 900 spectrophotometer and a Varian Cary 5000i with a 150 mm integrating sphere DRA were both used for the optical studies. Color calculations were carried out using Varian's Color Software (1976 CIE standards, a 10° observer angle, and a D65 illuminant). Film thicknesses were measured using a Veeco DekTak 150 v9 Mechanical Profilometer.

Electrochemistry. A nonaqueous Ag/Ag^+ (silver wire in 10 mM $AgNO_3$ in 0.1 M LITRIF/ACN) was used as the reference electrode for all electrochemical polymerizations and spectroelectrochemistry. The electrode was calibrated to be 0.456 V versus NHE using a ferrocene/ferrocenium couple. Electrochemical deposition of PT34bT, PEDOT, PProDOT-Me_2, and PDiBz-ProDOT onto ITO were carried out from 0.1 M LITRIF/ACN containing 10 mM monomer. Charge capacities were measured by switching the deposited polymer in 0.1 M LITRIF/ACN between −0.6 and 0.4 V for each of the electrochromic polymers and −0.7 and 0.5 V for the ion storage layer.

Solid State EC Windows. The devices were constructed by sandwiching a photocured gel-electrolyte[17] in between two 1.5 in. × 2 in. ITO coated glass pieces electrodeposited with the oxidized electrochromic film and a neutral film of PT34bT.

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Table 1. Representative Reactions for the Electrochromic Polymers Used in This Study

bleached state				colored State		
PDiBz-ProDOT^{n+}(nA$^-$)	+	ne^-	→	PDiBz-ProDOT^0		
PT34bT^0			→	PT34bT^{n+}(nA$^-$)	+	ne^-
PDiBz-ProDOT^{n+}(nA$^-$)	+	PT34bT^0	→	PT34bT^{n+}(nA$^-$)		PDiBz-ProDOT^0

The solid-state EC windows shown in Figure 5 are held at constant potentials of −1 and 1 V for the bleached and colored states, respectively.

Results and Discussion

Dual Polymer Electrochromic Devices Using PT34bT. The u′ and v′ values (1976 CIE standards) for PT34bT in both the bleached and colored states was calculated to be about 0.19−0.20 and 0.47−0.48, respectively. The u′ and v′ values for the 6000 K blackbody radiator (reference point) are 0.2033 and 0.4712. Both the neutral and oxidized PT34bT does not exhibit any coloration of its own and is close to that of the white reference point. The following half-reactions and overall redox reaction at the two electrodes coated with PDiBz-ProDOT and PT34bT depicts the concept of using very low band gap conjugated polymers with little or no visible electrochromism as the ion-storage layer. The reactions in Table 1 are representative for the electrochromic polymers used in this study.

Operating Potential Window. PT34bT and PDiBz-ProDOT were electrochemically deposited at 1.3 V (vs Ag/Ag$^+$). Dual polymer liquid cells comprised of PT34bT/PDiBz-ProDOT with matched charge capacities were constructed with PT34bT in the neutral state and PDiBz-ProDOT in the oxidized state using 0.1 M LITRIF/ACN as the electrolyte. Figure 3 shows the cyclic voltammogram for a PT34bT/PDiBz-ProDOT EC window for the first three cycles. After equilibrating at 0 V for 5 s, the scanning was started in the positive direction initially. The devices were found to exhibit a full switch between a potential of −0.8 and a potential of 0.8 V as compared to −1.5 and 0.9 V for a PDiBz-ProDOT dual polymer EC window using PBEDOT-NMCz as an anodically coloring polymer.[18]

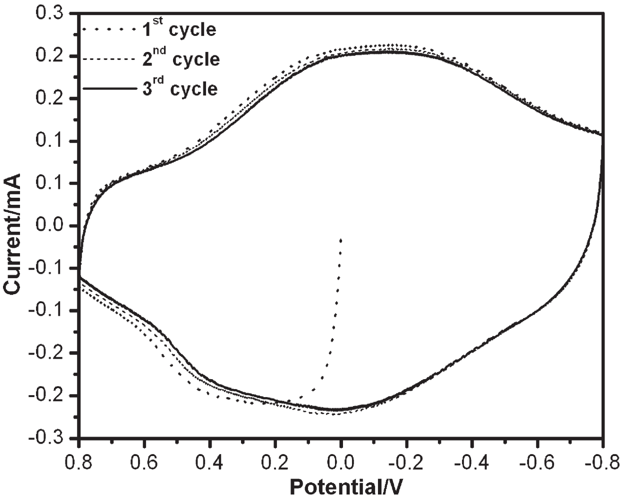

Figure 3. Cyclic voltammogram of a PT34bT/PDiBz-ProDOT dual polymer EC window. Potentials are referenced against the PDiBz-ProDOT coated electrodes; scan rate = 100 mV/s.

Optical Properties and Colorimetric Analysis. Much study has been carried out on materials such as PEDOT, PDiBz-ProDOT, and PProDOT-Me$_2$, and their devices are well documented.[18−24] To assess the use of PT34bT as a complementary electrode material for ECDs, we have synthesized our own chromophores. Dual polymer EC windows were constructed with oxidized PDiBz-ProDOT, PProDOT-Me$_2$, and PEDOT and neutral PT34bT. EQCM data from previous studies has determined a doping level for PT34bT to be near 27%. The levels for the chromophores were calculated to be 14%, 15%, and 18% for PEDOT, PProDOT-Me$_2$, and PDiBzProDOT, respectively. Thus, the constructed devices were made in such a way that the film thickness or charge per unit area of each layer was balanced. For every charge injected to the gel layer by one electrode, another charge should be absorbed by the layer on the opposite electrode. For comparative purposes, film thicknesses for each electrochromic polymer were optimized with respect to maximum photopic contrast. The optimum photopic contrast for PDiBz-ProDOT, PProDOT-Me$_2$, and PEDOT was achieved at a deposited charge capacity of approximately 0.91 mC/cm^2 (425 nm film), 1.39 mC/cm^2 (356 nm film), and 1.73 mC/cm^2 (340 nm film), respectively. Their resultant maximum photopic contrasts follow respectively 54%, 70%, and 57%. The films were prepared by solution state oxidative polymerization, and the contrast for a series of films was calculated from its absorption curves. The Supporting Information contains plots of contrast versus film thickness. Note that, for the noncoloring ion storage layer, PT34bT, the contrasts remain fairly low due to the lack of significant coloration. The film thicknesses of ion storage layer used were 210 nm, 194 nm, and 220 nm for PDiBz-ProDOT, PProDOT-Me$_2$, and PEDOT, respectively. The maximum expected loss of photopic contrast for these thicknesses is 9% (see Supporting Information). This furthers the applicability of the material, as even the thickest necessary depositions of the ion storage layer will not manifest as large color or contrast changes in the final device.

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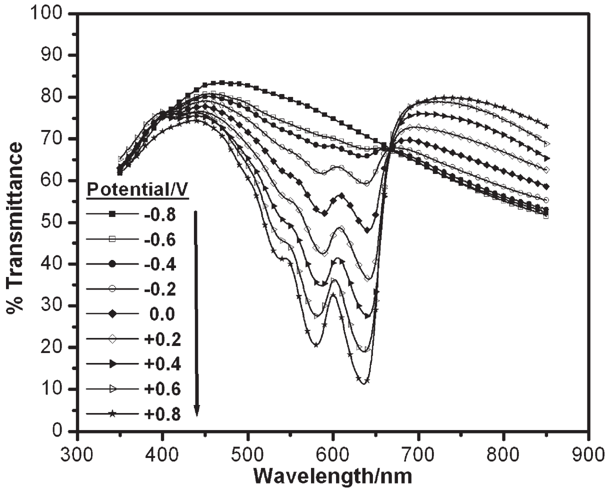

Figure 4. Representative visible transmittance spectra as a function of potential for a PT34bT/PDiBz-ProDOT EC window device.

Table 2. Bleached, Colored State Transmittance Values and Contrast (%Δ*T*) at the Peaks and the Photopically Weighted Transmittance Values of the PT34bT/PDiBz-ProDOT, PT34bT/PProDOT-Me$_2$, and PT34bT/PEDOT Dual Polymer EC Windows

electrochromic material	λ (nm)	bleached state (%)	colored state (%)	contrast (%ΔT)
PT34bT/PDiBz-ProDOT	579	77	21	56
	photopic	78	37	41
PT34bT/PProDOT-Me$_2$	577	65	2	63
	photopic	66	7	59
PT34bT/PEDOT	515	35	4	31
	photopic	29	2	27
PDiBz-ProDOT	579	78	15	63
	photopic	81	38	43
PProDOT-Me$_2$	577	83	5	78
	photopic	82	15	67
PEDOT	515	39	3	36
	photopic	37	3	34

The optical memory for all devices prepared was evaluated over a 30 min period using UV−vis analysis, and in all cases the devices were found to be stable (no loss of absorbance or contrast). The devices were stored overnight in a desiccator and retained their oxidation states over this time, as well (less than 1% change in transmission). Switching speeds were calculated by UV−vis analysi,s and it was found that the times were 1.2 s, 1.7 s, and 1.5 s with no PT34bT layer versus 0.9 s, 1.0 s, and 1.0 s with the ion storage layer, for PProDOT-Me$_2$, PEDOT, and PDiBz-ProDOT, respectively. The moderate enhancement of switching speeds with the addition of an ion storage layer can be attributed to proper ion shuttling. The long-term switching stability for each device has also been initially evaluated over the course of 50 cycles. It has been found that there is no significant difference between the devices over the first 50 cycles, as there was no observed loss of charge or contrast over this period.

Figure 4 *s*hows the change in the visible spectrum for a representative PT34bT/PDiBz-ProDOT device as a function of potential. The spectra shown herein are for the polymers alone with the absorbance of the other materials zeroed out as a blank, including the gel electrolyte. The dual polymer EC cell was a deep blue when the PDiBz-ProDOT layer is neutral (i.e., when PT34bT is in its oxidized state) and a transmissive sky blue when the PT34bT layer is neutral (i.e., when PDiBz-ProDOT is in its oxidized state). Hereafter, the terms "neutral state" and "oxidized state," when applied to devices, will refer to the chromophore layer and not the ion storage layer.

The bleached state, colored state, and contrast values for the devices prepared with and without PT34bT layers are summarized in Table 2. The color for the PEDOT/PT34bT device ($\lambda_{\max}$ = 593 nm, maximum contrast at 515 nm) ranges from a moderate blue colored neutral state to a transmissive sky blue colored oxidized state, while the colors of the PProDOT-Me$_2$/PT34bT device ($\lambda_{\max}$ = 593 nm, peaks at 544 and 623 nm, shoulder at 496 nm) goes from a deep purple in its neutral state to a similar transmissive sky blue in the oxidized form. Although the spectral sensitivity of the eyes is very broad, ranging between 400 and 800 nm, they are most sensitive at 555 nm. Again, it is not appropriate to report the values at single wavelengths for eye-wear applications and hence a photopically weighted measurement is needed. The photopic values in the bleached and colored states were calculated using the following equation and shown in Table 2.

$$T_{\text{photopic}} = \frac{\int_{380}^{720} T(\lambda)\, S(\lambda)\, P(\lambda)\, \mathrm{d}\lambda}{\int_{380}^{720} S(\lambda)\, P(\lambda)\, \mathrm{d}\lambda}$$

where $T(\lambda)$ is the spectral transmittance of the device under test, $S(\lambda)$ is the normalized spectral emission of a 6000 K blackbody, and $P(\lambda)$ is the normalized spectral response of the eye.

For translating the same or similar contrast within a device, a high transmissivity of the substrate and the gel electrolyte is required since the bleached state of the dual polymer EC window is not as high as that of the electrochromic polymers alone.

Nevertheless, the novel feature of this EC window configuration is that the color of the active electrochromic material is not significantly affected by the absorbance of PT34bT, both in neutral and oxidized states. This could be very useful in fabricating dual polymer full color displays, wherein very low band gap conjugated polymers can be used as the common ion-storage layer on the auxiliary electrode irrespective of the colors of the active polymer layer. PT34bT will act like a neutral density filter if held in front of the coloring polymer. Figure 5 shows the color trace of PDiBz-ProDOT in comparison with that of PT34bT/PDiBz-ProDOT dual polymer EC window as a function of potential, as well as images of the device and its control in their extreme color states. The comparisons of the color paths for PEDOT and PProDOT-Me$_2$ are in the Supporting Information.

The u′ and v′ values were calculated using a 6000 K blackbody radiator as the reference point. This color space was chosen because of its relevance to transmission-based devices, such as windows. For PDiBz-ProDOT, in the neutral blue state (−0.6 V, vs Ag/Ag$^+$) the u′ and v′ values are 0.1675 and 0.3982, respectively. In the oxidized transmissive sky blue state (0.4 V, vs Ag/Ag$^+$)

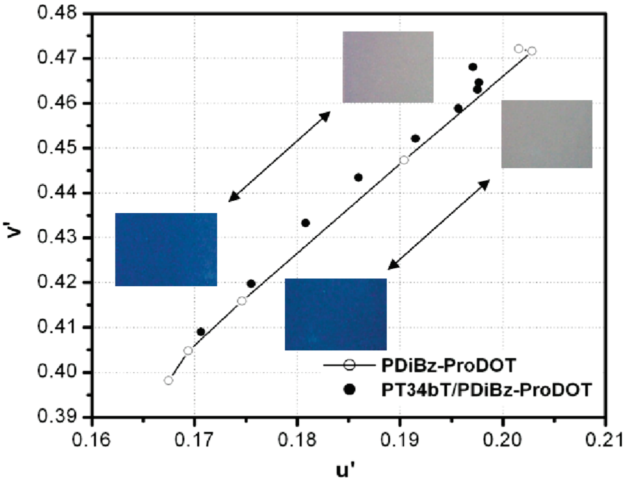

Figure 5. Transition of colors of electrochromic devices shown as CIE color space plots for PT34bT/PDiBz-ProDOT between −0.8 V and + 0.8 V (filled circles), PDiBz-ProDOT between −0.6 V and +0.4 V, (unfilled circles/line); values shows are using 1976 CIE color standards; all voltages are versus nonaqueous Ag/Ag$^+$ reference electrode. Color boxes are photographs of the devices in the extreme states (under the curve are with ion storage layer; over the curve are without ion storage layer).

the u′ and v′ values are 0.2015 and 0.4721, respectively. For PProDOT-Me$_2$, the neutral purple state had u′v′ values of u′ = 0.1802 and v′ = 0.3730 and the oxidized transmissive blue state had the pairing u′ = 0.1950, v′ = 0.4533. The PEDOT system had neutral state colors of u′ = 0.1913, v′ = 0.4552 and oxidized state colors of u′ = 0.1925, v′ = 0.4615. The luminance of the colors, as well as the photopic contrast of the devices, changed predictably with the introduction of the ion storage layer. This can be seen clearly by the values shown in Table 2, where a negative change in photopic contrast (going from devices without an ion storage layer to devices with an ion storage layer) of 2%, 8%, and 7% was observed for PDiBz-ProDOT, PProDOT-Me$_2$, and PEDOT devices, respectively. This is consistent with the expected loss of contrast due to the PT34bT itself, where a maximum loss of 11% (9% for the thicknesses used in these experiments) was predicted based on the contrast for various film thicknesses of the ion storage layer (see Supporting Information).

Conclusions

We have demonstrated the use of a low band gap conjugated polymer, PT34bT, as an ion-storage layer in electrochromic windows. PT34bT was found to exhibit a neutral sky blue in the undoped form and a colorless transmissive state in the oxidized form. Dual polymer EC windows comprised of PDiBz-ProDOT, PProDOT-Me$_2$, and PEDOT with PT34bT were constructed and characterized electrochemically, and their optical properties were evaluated. As was expected, the contrast of this EC window in the transmission mode was lowered but the yellow tinge associated with other reported ion storage layers, with yellow being known to distort color perception, was eliminated by the use of PT34bT. Furthermore, the CIE color plots and images indicate that in all cases studied the color of the active electrochromic polymer does not change significantly in the presence of PT34bT as the ion-storage layer on the auxiliary electrode. Thus, this dual EC window configuration using a very low band gap conjugated polymer, which is nearly colorless, could be useful for the fabrication of electrochromic eyewear, windows, or the blue component of a full color display.

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Supporting Information Available: Plots for the contrast versus film thickness of the materials used in this paper, as well as the spectroelectrochemistry and color coordinate plots for the secondary chromophores used (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.