High Contrast Ratio and Fast-Switching Dual Polymer Electrochromic Devices

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A series of dual polymer electrochromic devices (ECDs) based on 12 complementary pairs of conducting polymer films have been constructed using 3,4-ethylenedioxythiophene-containing conducting polymers. Poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-*N*-methylcarbazole] (PBEDOT-NCH$_3$Cz), poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-*N*-eicosylcarbazole] (PBEDOT-NC$_{20}$H$_{41}$Cz), and poly[4,4′-bis(2-(3,4-ethylenedioxythiophene))biphenyl] (PBEDOT-BP) were utilized as anodically coloring polymers that electrochemically switch between an oxidized deep blue absorptive state and a transmissive (orange or yellow) reduced state. Poly(3,4-ethylenedioxythiophene) (PEDOT) and its alkyl derivatives (PEDOT-C$_{14}$H$_{29}$ and PEDOT-C$_{16}$H$_{33}$) have been used as high-contrast cathodically coloring polymers that switch between a deep blue absorptive state in the reduced form and a sky blue, highly transmissive state in the oxidized form. The dual polymer ECDs were constructed by separating complementary pairs of EC polymer films, deposited on ITO glass, with a gel electrolyte composed of a lithium salt and plasticized poly(methyl methacrylate) (PMMA). Device contrast ratios, measured as $\Delta\%T$, ranged from 27% to 63%, and subsecond switching times for full color change were achieved. These devices were found to exhibit extremely high coloration efficiencies of up to 1400 cm^2/C over narrow (ca. 100 nm) wavelength ranges and to retain up to 60% of their optical response after 10 000 deep, double potential steps, rendering them useful for EC applications.

Introduction

Electrochromic devices (ECDs) may soon prove useful for a variety of switchable window, electromagnetic shutter and slow display technologies. ECDs that exhibit high contrast ratios ($\Delta\%T$) between their bleached and colored states are of special interest for use in dialed-tint windows, large area displays, and automatic dimming mirrors. In addition to optical contrast, fast response times will prove important for many applications. Three major classes of materials have evolved for incorporation into ECDs and are briefly described below.[1]

The first two categories of electrochromic (EC) materials are the molecular dyes and metal oxide films, respectively comprised of various organic and inorganic compounds. Molecular dyes can often be deposited as thin films onto optically transparent electrodes (OTEs) or can be dispersed throughout an electrolyte in an electrochemical cell. Dyes deposited as electrode-confined films can exhibit fast response times ranging from 20 ms (for Prussian Blue) to a few seconds, whereas the switching rates for those dispersed throughout an electrolyte are limited by diffusion to the electrode surface, therefore leading to a slower response. Using dispersed molecular electrochromics, ECDs have been constructed that are fully transparent with no

applied voltage and opaque dark green or blue upon the application of 1 V.[2] Metal oxide films are commonly prepared as the oxides of either tungsten, nickel, or molybdenum through the use of sol–gel, electrochemical, or sputtering techniques onto OTEs.[1,3] The behavior of metal oxide ECDs is dependent on pH, moisture, and exposure to the atmosphere.[4] Generally, the switching rates of crystalline metal oxide films are slow in comparison to electrode-confined films of molecular dyes, with response times on the order of 15–60 s required to achieve 100% conversion to either the colored or bleached state.[3,4]

Conducting polymers (CPs) comprised of a number of functionalized polypyrroles (PPy), polythiophenes (PT), polyanilines (PANI), etc., have become recognized as a third class of EC materials.[5] Film preparation usually entails the electrochemical polymerization of a monomer from electrolyte solution accompanied by the precipita-

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tion of the oxidized polymer onto an OTE. Functionalization of these polymers with solubilizing pendant groups affords EC materials that can be processed by common methods including spraying, printing, spin coating, or solution casting. For the case of aromatic conjugated polymers, oxidation induces a structural modification to a charged, and typically more planar, quinoidal backbone. The polymers' optical states are altered by creating electronic states with electronic transitions at lower energies than that exhibited by the π to π^* transition. By varying the electronic nature of the backbone, and the steric interactions between repeat units, the band gap (defined here as the onset of the π to π^* transition), and, ultimately, the coloration of the polymer can be tailored. Response times in these systems are governed by the diffusion of charge-compensating counterions through the thin films during redox switching. Quite often, the counterions have a high degree of mobility attributable to an open polymer morphology, thereby leading to enhanced optical response times of the ECDs.

ECDs prepared using CPs can be constructed by sandwiching a gel electrolyte between a CP deposited on an OTE and a bare OTE. A problem with this design is that degradative reactions of the electrolyte occur due to the absence of an effective counter-reaction. This limits lifetimes due to the build-up of degradation products in the cell. A design which counteracts this utilizes reversibly switchable CPs (or a combination of a CP with another EC material) at both electrodes of the ECD. For the case of a switchable window, this necessitates that one CP be anodically coloring while the other is cathodically coloring, allowing the device to switch between highly transmissive and absorptive states. Previously, we have communicated that high-contrast and rapidly switching ECDs can be constructed with this fabrication technique using complementary pairs of CPs specifically designed for this purpose.[6] In the past, a number of studies have been carried out on such devices combining CPs with other types of electrochromic materials.[7]

A diagram demonstrating the concept of complementary conducting polymers for use in dual polymer transmissive/absorptive ECDs is presented in Figure 1.

Ideally, an anodically coloring CP is chosen to have a high band gap (E_g) ≥ 3.0 eV (<410 nm) with π to π^* electronic transitions extending from the high-energy

end of the visible spectrum into the ultraviolet region, as illustrated by the dashed line in the top spectrum of Figure 1. In its reduced form, the polymer is transmissive to a major portion of the visible spectrum. Upon oxidation, charge carrier absorptions are induced in the visible region, as illustrated by the dashed line in the bottom of spectrum of Figure 1, resulting in an opaque and/or colored state. This anodically coloring behavior is observed for many of the common conjugated polymers, including poly(p-phenylene), polypyrrole, and poly(p-phenylene vinylene).

A complementary low band gap polymer is then selected with its gap energy close to the near-IR to visible transition of the spectrum (ca. 1.6 eV, 775 nm). As such, they are colored and opaque in the neutral state (see solid line in the bottom spectrum of Figure 1). Upon oxidation, lower energy transitions arise in the near-infrared region of the spectrum at the expense of the interband transition, which loses its intensity. Depletion of the absorption in the visible region causes the material to become transmissive and lightly colored (see solid line, top spectrum of Figure 1). Reduction of the oxidized form back to its neutral state returns the interband transition absorption and the material is cathodically coloring.

Initial construction of a dual polymer sandwich-type device, as shown schematically in Figure 2, is carried out with one polymer doped while the other is neutral, making both either transmissive or absorptive, and the device can be viewed as bleached or colored. Reversal of the bias potential oxidizes the neutral polymer with concurrent reduction (charge neutralization) of the oxidized polymer, inducing color formation, or bleaching. The ability to match the number of redox sites in each film leads to a high EC contrast in the device as the extremes of absorption and transmission can be attained.

Historically, poly(isothianaphthene) (PITN) was reported as the first example of a useful, low band gap, cathodically coloring CP.[8] For a number of synthetic and electrochemical reasons, PITN has not found a high level of applicability in ECDs. Recently, poly(3,4-ethylenedioxythiophene) (PEDOT) has emerged as a low band gap (E_g = 1.6 eV, 775 nm), cathodically coloring CP that can be prepared from the electrochemical or chemical polymerization of commercially available 3,4-ethylenedioxythiophene.[9] In addition to its low band gap, PEDOT has a low redox potential, is very stable to multiple redox switching, and has a high conductivity

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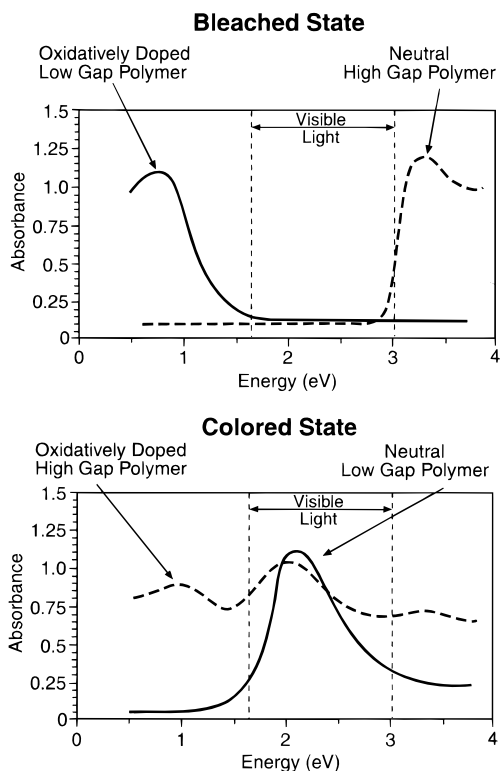
Figure 1. Schematic representation of the visible spectra for both an anodically and cathodically coloring polymer demonstrating the concept of dual polymer ECDs for absorptive/transmissive windows.

Figure 2. Schematic diagram of a dual polymer ECD sandwich cell with complementary cathodically and anodically coloring polymers.

Figure 3. The series of EDOT and BEDOT-arylene variable color electrochromic polymer films electrochemically deposited on ITO glass.

(200 S/cm). These properties are attributed to the high electron density of, and steric alleviation between, repeats contributed by the 3,4-fused dioxane ring. For these reasons, PEDOT and its substituted derivatives are excellent candidates for use in ECDs.[10]

In addition to the required complementary optical properties, proper ECD operation requires a high degree of electrochemical reversibility and compatibility. For example, with the exception of PPy, electropolymerized high gap CPs are prepared from monomers that oxidize at a high potential. Electrochemical polymerizations performed under extreme conditions often lead to the formation of defects and overoxidized material,[11] limiting electrochemical cyclability. We,[12] and others,[13] have overcome this problem by preparing monomers with extended conjugation using electron rich heterocycles as the terminal moieties to yield a broad class of easily prepared and switched polymers. Judicious choice of
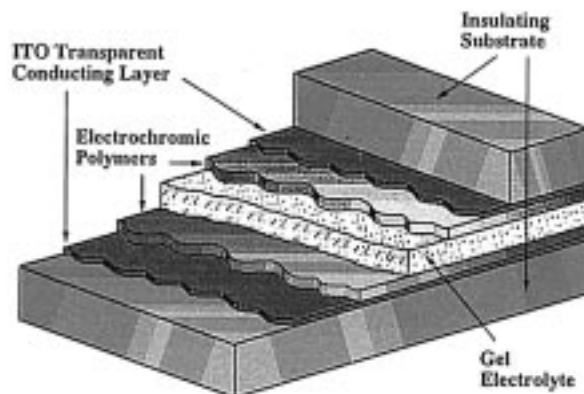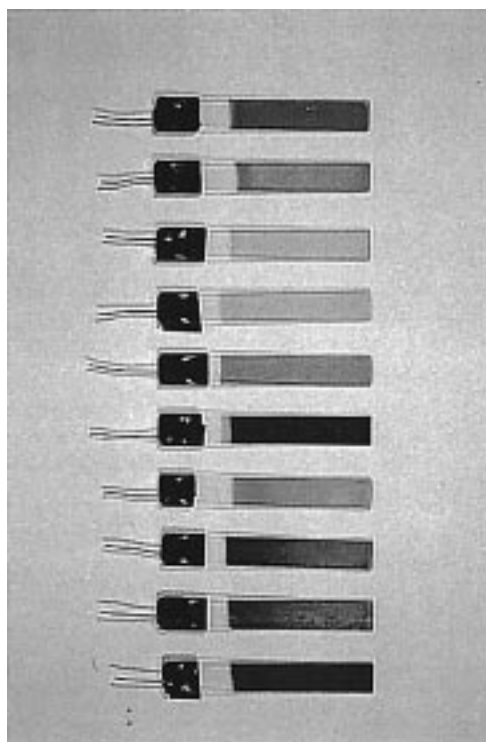
monomers yields anodically coloring polymers which are both optically complementary and electrochemically compatible in ECDs with the EDOT family of cathodically coloring polymers. Using this method, we have succeeded in attaining polymers with E_g values ranging from 1.1 to 4.0 eV, allowing us to prepare EC films of essentially any color. This is nicely illustrated by the photograph in Figure 3 which shows a series of electrochemically deposited polymer films of EDOT and bis-(2-EDOT)arylene (BEDOT-Ar). Note the accessible reds and oranges from the BEDOT-benzene and BEDOT-biphenyl, yellows and greens from the BEDOT-carbazoles, and blues from the parent EDOT family of polymers.

For the work reported here, we have designed and prepared a series of monomers containing terminal EDOT units that electrochemically polymerize at low

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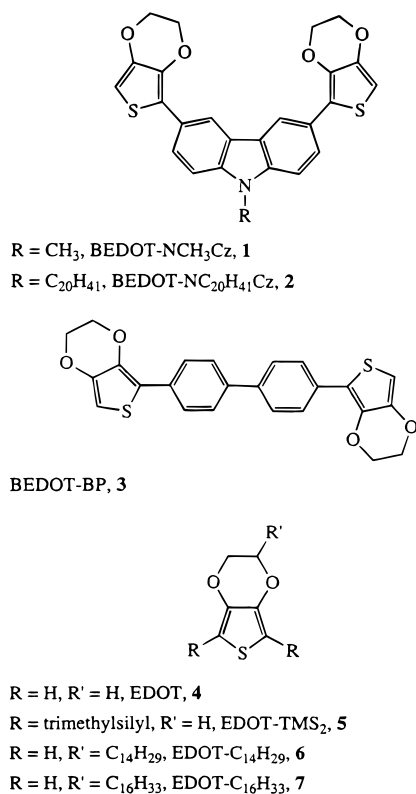
Figure 4. Monomers used for the preparation of both anodically coloring polymers (from the electrochemical polymerization of compounds **1** through **3**) and cathodically coloring polymers (from the electrochemical polymerization of compounds **4**–**7**).

oxidation potentials to yield a number of electrochromic CPs that are able to access a wide range of color states.[10a,10c,14] The monomers used in this study, 3,6-bis(3,4-ethylenedioxythiophene)-*N*-methylcarbazole (BEDOT-NCH$_3$Cz) (**1**), 3,6-bis(3,4-ethylenedioxythiophene)-*N*-eicosylcarbazole (BEDOT-NC$_{20}$H$_{41}$Cz) (**2**), 4,4′-bis(2-(3,4-ethylenedioxythiophene))biphenyl (BEDOT-BP) (**3**), EDOT (**4**), 2,5-bis(trimethylsilyl)-3,4-ethylenedioxythiophene (EDOT-TMS$_2$) (**5**), 2′-tetradecyl-3,4-ethylenedioxythiophene (EDOT-C$_{14}$H$_{29}$) (**6**), and 2′-hexadecyl-3,4-ethylenedioxythiophene (EDOT-C$_{16}$H$_{33}$) (**7**), are depicted in Figure 4. Compounds **1**–**3** are monomers that, when polymerized, yield anodically coloring CPs, whereas structures **4**–**7** yield cathodically coloring CPs. Using a number of combinations of CPs prepared from monomers **1**–**7**, we have constructed and tested a diverse series of dual-polymer ECDs that exhibit a broad color variation, can attain high EC contrast ratios, have subsecond response times, and retain 60% of their optical response after 10 000 deep, double potential steps. Coloration efficiencies (CEs) of four of the devices ranged from 421 to 1409 cm^2/C, indicating a very high EC efficiency.
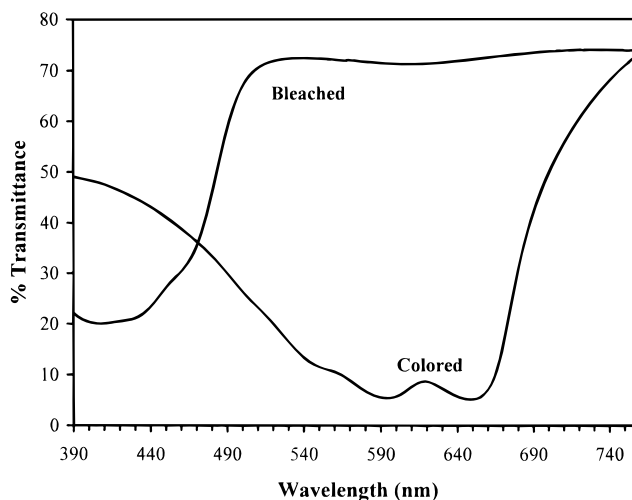
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Figure 5. Visible spectrum collected in transmittance mode of a PBEDOT-NCH$_3$Cz/PEDOT-C$_{16}$H$_{33}$ ECD in its fully transmitting and fully colored states.

Results and Discussion

Using the construction outlined in Figure 2, ECDs were prepared which consisted of a glass substrate coated with both an indium tin oxide (ITO) and a cathodically coloring EC polymer layer, poly(methyl methacrylate) (PMMA)/Li[N(SO$_2$CF$_3$)$_2$]/propylene carbonate (PC) gel electrolyte, and a second ITO-coated glass slide with an anodically coloring EC polymer. It should be noted that during the assembly of the ECDs, both polymers were in their opaque states. Evaporation of CH$_3$CN from the PMMA gel electrolyte led to PMMA precipitation at the device edges and provided a good seal, essentially creating a closed system.

After preparation, visible spectra of the ECDs between 390 and 800 nm were obtained. Figure 5 depicts the fully colored and bleached spectra of a PBEDOT-NCH$_3$Cz/PEDOT-C$_{16}$H$_{33}$ ECD and is representative for all of the devices reported herein. The photograph shown in Figure 6 demonstrates the optical contrast accessible by showing and hiding the cross printed on the paper under the device.

These two spectra show these two polymers to nicely complement one another to create a highly transmissive and opaque EC window as a function of the applied voltage potential. The spectrum depicting the deep blue colored state was obtained using an applied voltage at which the anodically coloring material, PBEDOT-NCH$_3$-Cz, was in its oxidized state and the cathodically coloring material, PEDOT-C$_{16}$H$_{33}$, was in its reduced state. Fundamentally, this spectrum constitutes the additive responses that both systems would exhibit separately. For example, PBEDOT-NCH$_3$Cz in the oxidized state exhibits one of its valence to charged state transitions at 590 nm, while neutral PEDOT-C$_{16}$H$_{33}$ exhibits three peaks which are centered at approximately 620 nm. It should be noted that the human eye is especially sensitive in the 550–650 nm region, making this device extremely sensitive visibly. When the opposite bias is applied, the ECD becomes highly transmissive between 490 and 760 nm. In this instance, the majority of the optical absorption at wavelengths less than 490 nm is due to PBEDOT-NCH$_3$Cz since it has a band gap of 2.5 eV (490 nm). As both of the
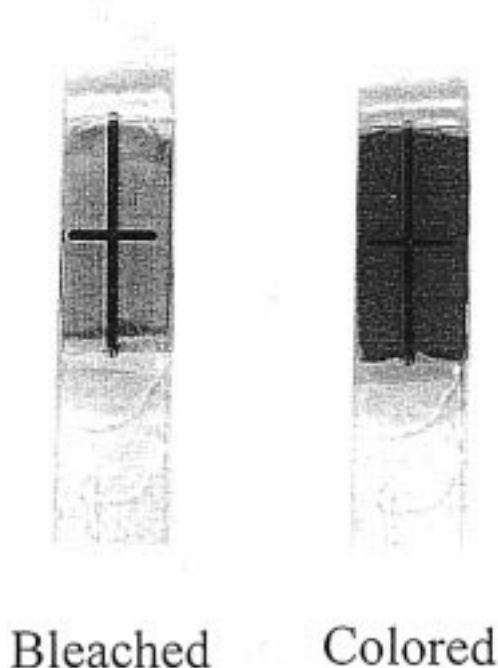
Figure 6. Dual polymer electrochromic device utilizing PEDOT-$C_{16}H_{33}$ (cathodically coloring) and PBEDOT-NCH_3Cz (anodically coloring) shown in fully bleached and fully colored states.

valence to bipolaron transitions of PEDOT-$C_{16}H_{33}$ are found in the near-IR region of the spectrum, they do not contribute to the absorption in the visible region. By selecting intermediate bias voltages, the color can be made to change as a variable tint colored to transmissive and the spectra evolve continuously from one extreme to the other. Generally, ECDs constructed using PBEDOT-NCH_3Cz as the anodically coloring polymer were transmissive yellow-green in the bleached state and blue to blue-violet in the opaque, colored state. Wavelengths for the maximum optical contrast (λ) varied from 550 nm for PBEDOT-NCH_3Cz/PEDOT or PEDOT-$C_{14}H_{29}$ to 650 nm for the PBEDOT-NCH_3Cz/PEDOT-$C_{16}H_{33}$ devices. This variation can be attributed to vibronic coupling in the neutral alkylated PEDOT derivatives. The splittings of the $\pi-\pi^*$ transition cause changes in the polymers' λ_{max} and, thus, alters the wavelength of maximum optical contrast. These results demonstrate the high ($\sim$60%) EC contrast ($\Delta\%T$) values attainable in the important region of the spectrum. Further work in our laboratory is directed to developing low oxidation potential (i.e., easily redox switched) high band gap polymers which will extend this high contrast over a broader spectral range.

To probe the switching characteristics of these ECDs, the transmission and attenuation of monochromatic light at the wavelength of maximum contrast was monitored during repeated redox stepping experiments. Figure 7 depicts the chronoabsorptometry results at maximum contrast for the redox switching of one of the PBEDOT-NCH_3Cz/PEDOT-$C_{16}H_{33}$ ECDs and is characteristic of all of the dual polymer ECDs reported. As shown, the percent transmittance of the device in the bleached state ($\%T_b$) is 68% and 8% in the opaque, colored state ($\%T_c$). This gives a difference in the percent transmittance ($\Delta\%T$) between the bleached and colored states of 60%. Contrast values and switching
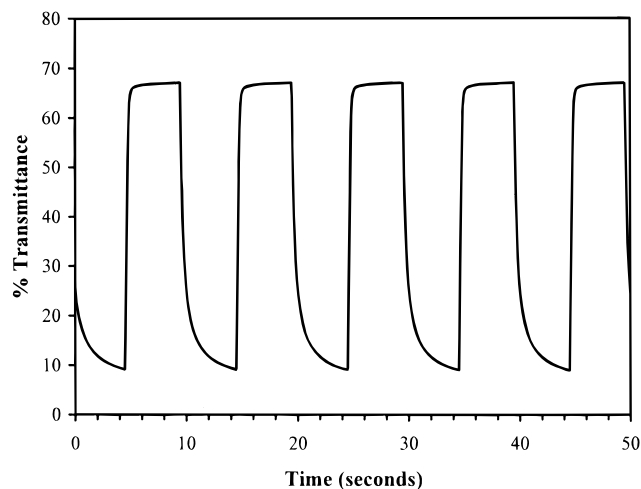

Figure 7. Electrochromic percent transmittance ($\%T$) results obtained for PBEDOT-NCH_3Cz/PEDOT-$C_{16}H_{33}$ ECD at $\lambda = 650$ nm with a 5 s delay for each potential ($\pm$0.9 V).

Table 1. Electrochromic Properties Obtained during Redox Stepping of a Series of Dual Polymer ECDs Using PBEDOT-NCH_3Cz as the Anodically Coloring Polymer

cathodically coloring polymer	λ (nm)[a]	$\%T_b/\%T_c$	$\Delta\%T$	t_b (s)	t_c (s)
PEDOT	550	68/21	47	0.20	0.30
PEDOT-TMS_2[b]	590	81/54	27	0.14	0.21
PEDOT-$C_{14}H_{29}$[c]	590	71/28	43	0.22	0.35
PEDOT-$C_{16}H_{33}$	650	68/5	63	0.32	0.64

[a] Wavelength of maximum optical contrast. [b] Values are listed as an average of three devices. [c] Values are listed as an average of two devices.

Table 2. Electrochromic Properties Obtained during Redox Stepping of a Series of Dual Polymer ECDs Using PBEDOT-$NC_{20}H_{41}Cz$ as the Anodically Coloring Polymer

cathodically coloring polymer	λ (nm)[a]	$\%T_b/\%T_c$	$\Delta\%T$	t_b (s)	t_c (s)
PEDOT	560	53/21	32	0.17	0.30
PEDOT-TMS_2	550	64/29	35	0.13	0.23
PEDOT-$C_{14}H_{29}$	550	45/9	36	0.27	0.47
PEDOT-$C_{16}H_{33}$	550	45/9	36	0.30	0.70

[a] Wavelength of maximum optical contrast.

response times for devices using PBEDOT-NCH_3Cz as the anodically coloring polymer are listed in Table 1. Response times for achieving the bleached state (t_b) and opaque, colored state (t_c) were determined as the time it took to effect 75% of the ultimate change in $\%T$. All of these devices exhibited quite fast response times of under 1 s. While in each instance the coloration process was slightly slower than the bleaching process, at this time no definitive mechanism can be proposed which adequately explains this. In this set, it can be seen that the ECDs utilizing PBEDOT-NCH_3Cz as the anodically coloring material and PEDOT-$C_{16}H_{33}$ as the cathodically coloring material exhibited the highest optical contrast of all the dual polymer ECDs.

A compilation of the optical contrast and switching response time results obtained for ECDs utilizing PBEDOT-$NC_{20}H_{41}Cz$ and PBEDOT-BP as the anodically coloring EC materials are given in Tables 2 and 3, respectively. Examining general trends reveals that the $\Delta\%T$ values are in the same range as those reported in Table 1. The highest $\Delta\%T$ values are seen when using the alkyl-substituted PEDOT derivatives as cathodically

Table 3. Electrochromic Properties Obtained during Redox Stepping of a Series of Dual Polymer ECDs Using PBEDOT-BP as the Anodically Coloring Polymer

cathodic polymer	λ (nm)[a]	$\%T_b/\%T_c$	$\Delta\%T$	t_b (s)	t_c (s)
PEDOT	605	50/21	29	0.10	0.30
PEDOT-TMS$_2$	600	61/34	27	0.07	0.17
PEDOT-C$_{14}$H$_{29}$[b]	635	76/17	59	1.50	0.48
PEDOT-C$_{16}$H$_{33}$[c]	650	63/14	49	0.24	1.20

[a] Wavelength of maximum optical contrast. [b] Values are listed as an average of two devices. [c] Values are listed as an average of four devices.
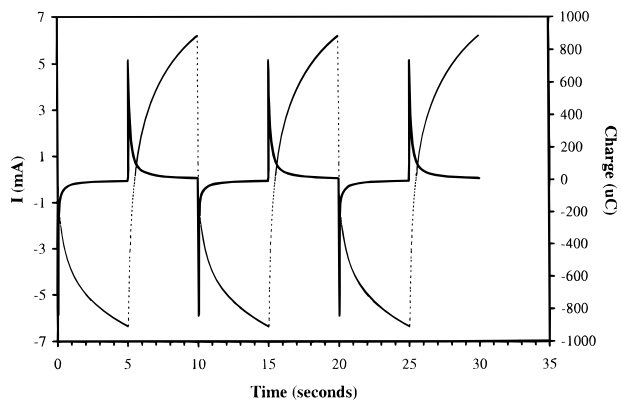

Figure 8. Chronoamperometry (solid line) and chronocoulometry (broken line) for PBEDOT-NCH$_3$Cz/PEDOT-C$_{16}$H$_{33}$ with a 5 s delay for each potential (±0.9 V).

coloring materials, due to their deep absorption in the reduced form. Use of unsubstituted PEDOT (prepared from either EDOT or its bis-TMS derivative) leads to lower contrast, as the dynamic range accessible is lower in the unsubstituted polymer. This can be attributed to the strong NIR tail that extends into the visible region for the oxidized form of the unsubstituted polymer. The important repression of absorption at 1.2–1.6 eV for the alkyl derivatized polymers increases their EC contrast.

One of the benefits of using the complementary paired polymers in combination with the gel electrolyte is fast switching response times for all systems. As evident in Tables 1–3, most of these ECDs exhibited subsecond switching times and in some instances were able to attain 75% of their optical change in 0.1 s or less. This is important when making comparisons to metal oxide and solubilized dye based ECDs, where switching times are much longer, as discussed earlier.

These devices were further characterized electrochemically by chronoamperometry and chronocoulometry in order to determine their electrical requirements for use. Chronoamperometry was carried out by monitoring device current response as a function of time while the applied voltage was stepped between +900 mV and −900 mV with a delay time at each voltage of 5 s. Chronocoulometric results were obtained through the integration of the current as a function of time and are shown for a PBEDOT-NCH$_3$Cz/PEDOT-C$_{16}$H$_{33}$ ECD in Figure 8. These results are representative of the data obtained for the other dual polymer ECDs. In these devices, the current requirements are on the order of a few mA/cm^2, which is similar to other CP-based devices reported.[7g] At the same time, it should be noted that these current requirements are lower than for many metal oxide based devices,[4a] indicating one of the beneficial properties of CPs.

Electrochromic memory, defined as the ability of an ECD to hold its color and/or optical density with the current off, is a practically important parameter when considering many applications. We find that, while a permanent memory effect was not observed for these devices, an optically intermediate state, usually close to the bleached state, is attained within 24 h at open circuit. As this is a slow loss, it is conceivable that the desired optical state could be maintained by occasional current pulses to freshen either the fully colored or highly transmitting states.

Coloration Efficiency. A key parameter used for comparisons between electrochromic materials is the coloration efficiency (CE). This is obtained by determining the injected/ejected charge as a function of the electrode area (Q_d) and the change in optical density (ΔOD) during a redox step of the device.[15] ΔOD at a given wavelength is expressed as

$$\Delta OD(\lambda) = \log[T_b(\lambda)/T_c(\lambda)]$$

and the CE at the specified wavelength is expressed as

$$CE(\lambda) = \Delta OD(\lambda)/Q_d$$

For amorphous tungsten trioxide (WO$_3$) films fabricated by thermal evaporation, a CE of 115 cm^2/C (633 nm) can be achieved,[16] whereas polycrystalline morphologies created by sputtering lead to a CE of 42 cm^2/C.[17] The most widely investigated anodically coloring metal oxide is iridium dioxide (IrO$_2$), which exhibits a color change from transparent to blue-black. Both sputtered IrO$_2$ (SIROF) and anodic IrO$_2$ (AIROF) exhibit CEs of 15–18 cm^2/C.[18] Conducting polymers tend to exhibit higher CE values due to lower power requirements. CP films are more porous, allowing for facile diffusion of counterions during the doping and undoping processes. Poly(bithiophene) and poly(3-methylthiophene) electrochemically prepared on ITO glass and redox stepped in propylene carbonate/lithium perchlorate electrolyte were reported to exhibit CEs of 110 and 240 cm^2/C, respectively.[19]

Complementary mode ECDs utilizing poly(aniline) as the anodically coloring material and WO$_3$ as the cathodically coloring material have been reported previously.[20] A reported electrochromic efficiency of 170 cm^2/C was exhibited by such a device in a solid-state configuration using PMMA/LiClO$_4$ as the gel electrolyte.[20c] A liquid-based complementary mode ECD utilizing poly(pyrrole) as the anodically coloring material and WO$_3$ was reported to exhibit a CE of 123 cm^2/C.[21]

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Table 4. Charge Requirements, Optical Density Changes, and Coloration Efficiencies for Dual Polymer ECDs

anodic CP	cathodic CP	Q_p (mC)	area (cm²)	Q_d (mC/cm²)	ΔOD	CE (cm²/C)
PBEDOT-NCH₃Cz	PEDOT	1.37	1.13	1.21	0.51	421
PBEDOT-N CH₃Cz	PEDOT-C₁₄H₂₉	3.01	6.75	0.45	0.51	1133
PBEDOT-N CH₃Cz	PEDOT-C₁₆H₃₃	0.91	1.13	0.80	1.13	1413
PBEDOT-BP	PEDOT-C₁₆H₃₃	0.87	1.50	0.58	0.65	1121

Table 4 lists the CEs obtained for four of the dual polymer ECDs. The highest CE of 1409 cm²/C was obtained for the PBEDOT-NCH₃Cz/PEDOT-C₁₆H₃₃, while the lowest CE of 421 cm²/C was obtained for the PBEDOT-NCH₃Cz/PEDOT ECD. These results demonstrate the highly useful properties of the EDOT family of polymers for electrochromics. The combination of the high visible absorbance of the neutral state (common in conjugated polymers), the unique high degree of transmissivity of the doped state, and the ease of switching due to a low redox potential causes the device CEs to be extremely high. Such large CEs make these ECDs competitive with the complementary mode ECDs mentioned previously. The structural variations made possible by the bis-EDOT-arylene class of polymers then yield the full spectrum colors and allows multicolored variable tint ECDs to be prepared.

Long-Term Stability. Quite often the stability of the bleached and/or colored states toward multiple redox steps limits the utility of EC materials in ECD applications. Two problems encountered in combining two complementary coloring EC materials is that they often have different electrochemical windows and/or environmental requirements. If the two EC materials exhibit quite different electrochemical windows for operation, then the applied voltage in order to effect 100% of the optical contrast increases. EC materials that are able to operate at low applied potentials allow longer device lifetimes, since high applied potentials are degenerative to the electrochromic film, the ITO layer, the polymeric electrolyte, and the interfacial chemistry between each of these materials (e.g., causing delamination). To maintain charge balance within the ECD, the oxidation process of the anodic EC material should coincide with the reduction process of the cathodic EC material.

The dual polymer ECDs reported herein possess the ability to operate at low applied voltages with both films being compatible in the same electrochemical environment. Long-term redox switching stability studies were performed by continuously stepping the voltages of the devices between −900 mV and +900 mV with a 5 s delay at each potential. Devices were kept in the spectrophotometer during the stability experiments, and the transmittance was monitored as a function of time for up to 10 000 double potential steps. Figure 9 shows transmittance results for a representative long-term redox stepping experiment performed on a PBEDOT-NCH₃Cz/PEDOT-C₁₆H₃₃ ECD at $\lambda = 650$ nm. It can be seen that this device is relatively stable to attaining its highly transmissive state, yet begins to lose its deep color during the high number of switches. Generally, it was found that these ECDs were able to retain approximately 60% of their optical response after 10 000 deep double potential steps. Also, the data shown in Figure 9 shows that a 5 s potential step provides adequate time for an optical steady state to be achieved, thus confirming that the long-term stability studies were conducted for a "full" cycle.
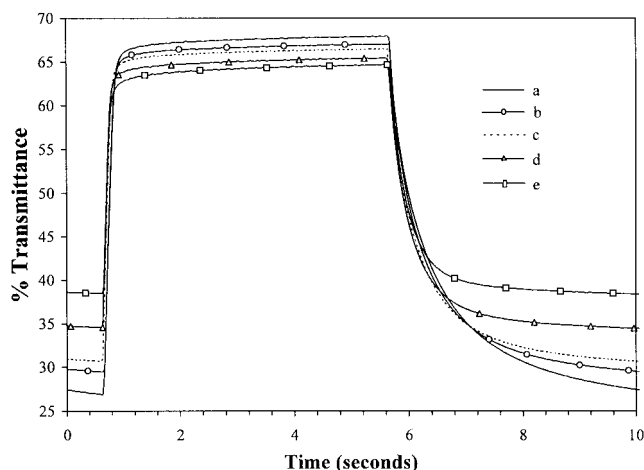

Figure 9. Long-term redox stepping results showing %*T* changes during double potential stepping at (a) 1 (b) 500 (c) 1000 (d) 5000, and (e) 10 000 double potential steps. This experiment was performed on a PBEDOT-NCH₃Cz/PEDOT-C₁₆H₃₃ ECD at $\lambda = 650$ nm with a 5 s delay for each potential (±0.9 V).

Experimental Section

Chemicals. Reagent grade ACN and PC were purchased from Fisher. ACN was distilled over calcium hydride and PC was percolated through activated type 3A molecular sieves (Aldrich), followed by vacuum distillation and storage under argon. Tetrabutylammonium perchlorate (TBAP) was purchased from Aldrich, recrystallized from ethanol, dried under vacuum at 50 °C for 24 h, and stored under argon. PMMA (Aldrich, $M_w = 996\ 000$) and Li[N(SO₂CF₃)₂] (3M) were dried under vacuum at 50 °C for 12 h and stored under argon prior to use. The monomers were obtained as follows: EDOT was obtained from AG Bayer; EDOT-TMS₂,[14e] EDOT-C₁₄H₂₉,[10a,c] EDOT-C₁₆H₃₃,[10c] BEDOT-NCH₃Cz,[14c,d] BEDOT-NC₂₀H₄₁Cz,[14c,d] and BEDOT-BP[14a] were prepared according to methodologies previously reported.

Gel Electrolyte Preparation. An electrolyte casting solution was prepared by adding ACN and PC via syringe to an argon-purged flask containing PMMA and Li[N(SO₂CF₃)₂]. This solution was stirred vigorously for 12 h, resulting in a gel with a weight percent composition of 70:20:7:3 (ACN:PC:PMMA:Li[N(SO₂CF₃)₂]).

EC Polymer Film Preparation. Polymer films were obtained by constant potential oxidative polymerization at potentials slightly higher than the monomer oxidation onset potential in order to obtain thin films on ITO electrodes. We found this to be the best method for obtaining films of high optical quality. Film thicknesses ranging from 0.06 to 0.20 μm were controlled by monitoring the total charge passed per unit area. Film thicknesses were measured by profilometry. Rates of polymer deposition varied for each material and were observed to be fastest for **1** and slowest for **4**. The film-bearing electrodes were removed from the monomer/electrolyte solution after electrochemical polymerization and placed into monomer-free electrolyte solution. The films were electrochemically conditioned by cyclic voltammetry between −0.90 and 0.90 V vs Ag/Ag⁺ for 20 cycles, ensuring that a maximum doping level would be accessible. Cathodically coloring films were fully reduced and anodically coloring films were fully oxidized before rinsing with ACN in order to maintain charge state balance before assembly into the ECDs.

Device Assembly. The ITO-coated glass substrates, covered with the appropriate EC polymer, were removed from the electrolyte solution and rinsed with freshly distilled ACN. Wet films were drip coated via syringe with gel casting solution until the entire polymer surface was covered. These substrates were then dried with a continuous flow of dry nitrogen gas for a period of 30 min. The selected cathodically and anodically coloring electrodes were then carefully applied to one another such that the films were contained between the glass and separated by ca. 0.5 μm. The assembled devices were then allowed to dry for 48 h, allowing the gel electrolyte to form a seal around the outer edges.

Electrochemistry. Electrochemical polymerizations were carried out using 10 mM monomer/0.1 M TBAP/ACN solutions with the exception of **1**, **2**, and **3**. These solutions were saturated with monomer (<10 mM) due to their limited solubility in ACN. A three-electrode cell configuration was used for all polymerizations. This consisted of an ITO-coated glass plate (working electrode), a 6.25 cm² sheet of stainless steel (counter electrode), and a Ag/Ag$^+$ nonaqueous reference electrode. The Ag/Ag$^+$ reference electrode contained a solution of 0.01 M AgNO$_3$/0.10 M TBAP which was calibrated using a ferrocene standard solution (0.005 M ferrocene, 0.1 M lithium perchlorate) and found to be 0.473 V vs the normal hydrogen electrode (NHE). All electrochemical solutions were purged with argon prior to use, and an argon blanket was maintained over the solution during experimentation. The stainless steel electrode was polished with steel wool, wiped with a tissue,

and rinsed with ACN prior to each usage. ITO-coated glass slides (sheet resistance = 40 Ω/cm²) were purchased from Delta Technologies Ltd. and received as a donation from Gentex Corp. These were treated prior to use by sonication in ACN. The dual polymer ECDs were electronically controlled by potentiostat in a two-electrode configuration.

Instrumentation. An EG&G Princeton Applied Research Model 273 potentiostat/galvanostat was used for all electrochemical experiments. UV−vis−NIR results, including in situ spectroelectrochemistry, were obtained using a Varian Cary 5E UV−vis−NIR spectrophotometer. Film thickness was determined using a Sloan Dektak II (profilometer).

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