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Plastic Electrochromic Devices: Electrochemical Characterization and Device Properties of a Phenothiazine-Phenylquinoline Donor−Acceptor Polymer

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We describe the morphological, electrochemical, spectroelectrochemical characterization, and electrochromic device properties of films of poly(2,2′-[10-methyl-3,7-phenothiazylene]-6,6′-bis[4-phenylquinoline]) (PPTZPQ). Cyclic voltammograms of PPTZPQ polymer films showed reversible electrochemical oxidation accompanied with a color change that was switchable as a function of the potential. However, the reduction behavior of PPTZPQ was unstable and caused a loss of the electrochromic effect. The spectroelectrochemical behavior of PPTZPQ was interpreted as the combination of the properties of the constituent donor and acceptor moieties. Two PPTZPQ solid-state electrochromic devices were constructed using indium tin oxide (ITO) deposited on polyester and poly(ethylene oxide) as a polymeric electrolyte. The electrochromic active materials were PPTZPQ as the primary electrode and ladder poly(benzobisimidazobenzophenanthroline) (BBL) or vanadium pentoxide (V_2O_5) as the secondary electrode. The PPTZPQ−BBL and PPTZPQ−V_2O_5 devices showed black-red and yellow-red color changes, respectively, during potential cycling.

Introduction

We report here the morphological, electrochemical, and spectroelectrochemical studies of poly(2,2′-[10-methyl-3,7-phenothiazylene]-6,6′-bis[4-phenylquinoline]) (PPTZPQ, Figure 1), an acceptor−donor (A/D) conjugated polymer. We also describe the construction and characterization of the electro-optical properties of two all-polymeric electrochromic devices using PPTZPQ as one electrode and ladder poly(benzobisimidazobenzophenanthroline) (BBL, Figure 1) or vanadium pentoxide (V_2O_5) as the counter electrode.

A reversible electrochemical process producing a color change resulting from the generation of new electronic absorption transitions in the visible region within a material is known as electrochromism.[1,2] An electrochromic device (ECD) is formed by a cell consisting of at least one optically transparent electrode (OTE), separated by a solid (often polymeric) gel or liquid electrolyte from a counter electrode. The electrochromic material (EM) can be present in the electrolyte or in the form of a film on the OTEs. A quantity of charge is reversibly exchanged between the working electrode (primary electrode) and a counter electrode (secondary electrode) by applying an external potential resulting in a cyclic color change.[3] The secondary electrode, in electrochromic terms, can either be optically neutral or switch in a complementary mode to the working electrode (e.g., the counter electrode is anodically colored, whereas the working electrode is cathodically colored).

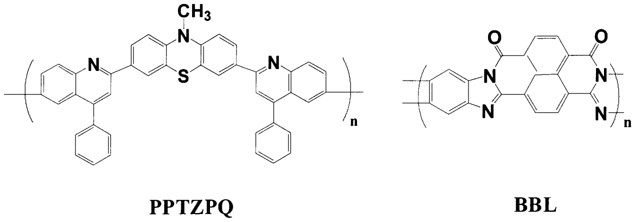

Figure 1. Polymer structures.

The potential uses of these types of devices are very broad, for example, electrochromic windows that control the radiant energy transfer in buildings and cars, improvement of energy efficiency,[1,3] electrochromic rear-view mirror systems in cars, thin flat panel displays, and smart paint and camouflage. These applications have led to a demand for new materials with improved electrochromic responses.[4] Many different types of materials have been described and used in the construction of electrochromic devices, such as inorganic systems based on transition metal oxides (e.g., WO_3,[5] V_2O_5,[6,7]

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and TiO$_2$[8]) and organic systems based on viologen, anthroquinone, and phenazine derivatives.[3,9,10] A few of the above materials provide the variable geometry and flexible properties needed in some electrochromic applications. There is current interest in the use of polymeric materials where more flexibility in the molecular design, higher molar absorptivity, lower production costs, and more appropriate mechanical properties (e.g., flexibility of films) are possible.

Electrochromic polymers must show reasonable electronic conductivity and band gap energies in the desired region of the electromagnetic spectrum. For example, low band gap polymers with absorption bands in the near-infrared region can be obtained by maximizing the π-electron delocalization within the conjugated polymer backbone through aromatic and quinoid-type structures with coplanar conformations between the polymer's consecutive repeat units.[11a−c,12a] Another strategy employed in producing conjugated polymers with controlled band gaps and electronic structures involves constructing A/D type polymers, where the A and D units are strong electron-withdrawing moieties and electron-donating moieties, respectively.[12a,b,13,14] An appropriate choice of the A and D units allows control of the energies of the π-system's effective HOMO and LUMO levels, which determine the polymer's oxidative and reductive properties. Consecutive A/D arrangements permit a high degree of intramolecular charge transfer (ICT) within the conjugated framework of the polymers.[13,15] This intramolecular charge transfer produces a successive zwitterion-like interaction with a high double-bond character between the repeat units. Common examples of polymers used in polymeric electrochromic devices include polyaniline,[16−18] polythiophenes,[19,20] and polypyrroles.[21]

Experimental Section

Materials. All the chemicals and solvents used in this work were commercial reagent grade.

The synthesis and characterization of the PPTZPQ and BBL polymers have been described elsewhere.[22,23] Solutions of PPTZPQ and BBL were 0.6 and 0.4 wt % in nitromethane/GaCl$_3$, respectively, and were prepared in an inert atmosphere inside a drybox.

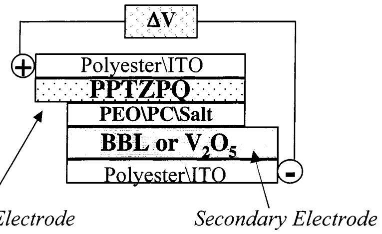

Figure 2. Electrochromic cell.

The V$_2$O$_5$ gels were prepared by protonation of sodium metavanadate via the sol−gel route;[6,7] 0.1 M sodium metavanadate was first prepared in Milli-Q water and then passed through an ion exchange column containing DOWEX 50WX2-200 resin. Protonation was achieved via ion exchange. Light yellow-colored decavanadic acid turned dark red in a few hours and formed red precipitates upon aging. The entire sol became a homogeneous gel within a few weeks. The V$_2$O$_5$ gel was aged at room temperature for at least 3 months to ensure homogenization before electrodes were prepared for electrochemical studies.

Optically transparent electrodes were cut from ITO-coated polyester (40−60 ohm/□) sheets, obtained from CPFilms Inc., Canoga Park, CA. The ITO electrodes were cleaned by sonication for 30 min in a 20 vol % solution of ethanolamine in Milli-Q water and then rinsed several times with deionized water to remove traces of ethanolamine.

Polymer and V$_2$O$_5$ Films Preparation. The PPTZPQ and BBL polymer films were prepared using a spin-coating system installed inside a drybox. A volume of 0.2 mL of polymer solution was spread onto a ~1-cm^2 ITO surface at 2000 rpm for 30 s. The polymer films were then put into a *N*,*N*-dimethylformamide (DMF) bath for 30 min to remove GaCl$_3$. Finally, the films were dried in a vacuum oven at ~70 °C overnight. The connection to the ITO was made by welding a metal wire in a polymer-free zone of the ITO surface with an indium droplet.

The V$_2$O$_5$ films were prepared by spin coating the gel in air onto an ITO substrate. A volume of 0.2 mL of V$_2$O$_5$ gel was spread onto a ~1-cm^2 ITO surface at 2000 rpm for 30 s. The plastic ITO electrodes were treated with 0.1 M NaOH for 20 min and then rinsed with water. These procedures improve the interaction between the oxide and the surface of ITO, resulting in more homogeneous films.

Preparation of Plastic Spectroelectrochemical Cells. Two electrochromic devices were constructed (a cross section is shown in Figure 2), one formed from PPTZPQ−BBL and the other from PPTZPQ−V$_2$O$_5$; in both cases, the electrodes were separated by a polymeric electrolyte. The electrodes were cycled in a supporting electrolyte (0.1 TBAPF$_6$ or LiClO$_4$ in propylene carbonate, (PC)) over the range of potentials where their electrochromic response is seen, before assembly of the cell. The V$_2$O$_5$ films were treated in the LiClO$_4$ in PC at a cathodic potential to intercalate lithium ions into the films. The light brown color of V$_2$O$_5$ film turned light blue after the lithium intercalation. The potential cycling was stopped when we observed stability in currents and homogeneity in the color film. The cell was immediately assembled, as is indicated in the next section.

The polymeric electrolyte was prepared in a drybox. The poly(ethylene oxide) (PEO) (average molecular weigh 4×10^6) solution was made by dissolving PEO in MeCN with LiClO$_4$ and PC as a plasticizer in a weight ratio 1:83:0.62:0.83 and then mechanically stirring overnight to obtain good homogeneity. Films were cast by pouring solutions into a flat glass container inside a hermetic box operated under a stream of nitrogen to completely evaporate the MeCN. Mechanically stable, free-standing films (~500-μm thick) were peeled from the glass surface.

The PPTZPQ−BBL and PPTZPQ−V$_2$O$_5$ cells were mounted by sandwiching the polymer electrolyte between the two

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electrodes. The electrodes were then pressed together until the polymeric electrolyte adhered to both electrodes. Finally, the electrochromic cells were sealed with adhesive tape.

Characterization. Electrochemical experiments were conducted with a CHI 660 electrochemical workstation (CH Instruments, Austin, TX) employing a three-electrode cell. The electrochemical cell and the electrolyte solution were maintained inside a drybox or under constant argon bubbling to avoid contamination by oxygen or water.

The electrolyte solution as a supporting electrolyte consisted of a benzonitrile and PC solution with 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$). The polymer is insoluble in these solvents, so the polymer film remained intact across a broad range of potentials during the electrochemical experiments. A platinum coil was used as the counter electrode, and a silver wire was used as a a quasi-reference electrode, which was calibrated vs SCE by the addition of ferrocene as an internal standard using $E^\circ_{(Fc/Fc^+)} = 0.324$ vs SCE.[24]

Spectroelectrochemical experiments were carried out in a homemade Teflon cell with quartz windows. ITO-coated glass was used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl wire as the quasi-reference electrode. The cell was placed in the optical path of the sample light beam in a Milton Roy Spectronic 3000 array spectrophotometer. The background correction was obtained by taking a UV/vis spectrum of a blank cell (an electrochemical cell with an ITO working electrode but without the polymer coating) with conditions and parameters identical to those of the polymer experiment.

Imaging experiments were performed with a Nanoscope II (Digital Instruments, Santa Barbara, CA) AFM in air at room temperature and atmospheric pressure. The images were not digitally filtered. The sample was manually positioned below the tip and maintained perpendicular to the sample surface through the microscope adjustment screws. Part of the film was removed from the ITO surface with a razor blade in the study to determine the film thickness with a profilometer (Tencor Instruments, model: Alpha-Step 100).

The experimental setup for SECM measurements has been previously described.[25−27] Potentiostatic experiments of the polymer-covered substrate were performed with 1 mM methyl viologen (MV) as the mediator in 0.1 M $TBAPF_6$ in PC. The solutions were bubbled with Ar before the SECM experiments, and during the measurements, the cell was maintained under an Ar atmosphere. A CHI 630 electrochemical workstation was used for the tip characterization in the absence of the polymer substrate.

Resistance measurements in solution were performed as previously described.[25,26] This method used a four-microband-electrode array covered by the film (obtained by spin coating). The resistance measurement was performed with a dc voltmeter connected between the two central microbands, while the potential applied to the external microbands was varied.

Results and Discussion

Electrochemical Characterization. Voltammetric studies were performed in 0.1 M $TBAPF_6$ in either benzonitrile or PC. In these solvents we found a well-swollen film, contrary to MeCN where the film did not show a good electrochemical response. In both solvents the PPTZPQ films showed similar electrochemical characteristics. To characterize the ITO films on polyester plastic as electrodes, we studied the electrochemical response of ferrocene in MeCN and obtained the same behavior as with ITO on glass. Similarly, the electrochemical characteristics of PPTZPQ on polyester\ITO and glass\ITO were not significantly different.

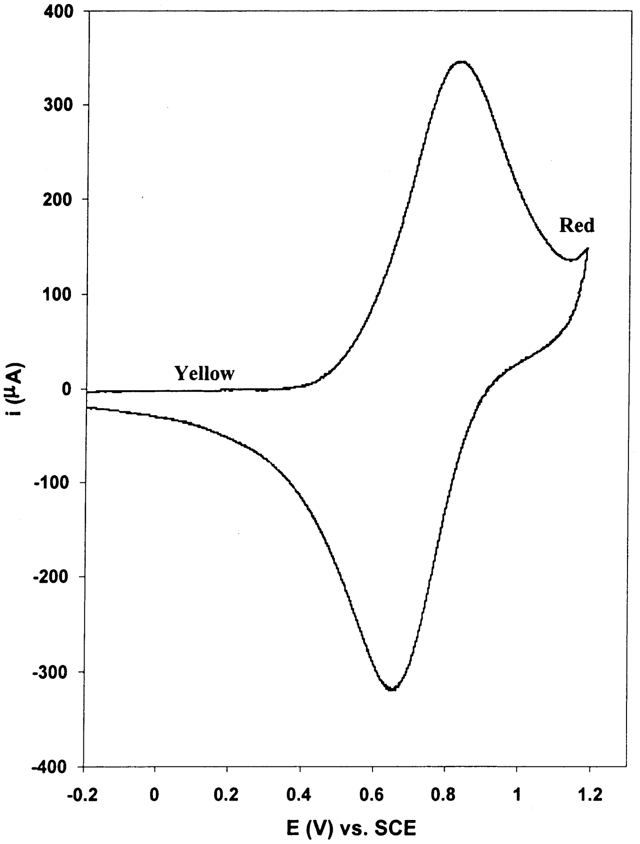

Figure 3. Cyclic voltammetry of oxidation of a 0.62-μm-thick PPTZPQ film spin-coated over an ITO electrode with PC containing 0.1 M $TBAPF_6$ as the supporting electrolyte. Scan rate 50 mV/s.

The PPTZPQ film shows cathodic and anodic responses with a clear and homogeneous change of color from yellow to red in the anodic region. A voltammogram of a PPTZPQ spin-coated film over plastic/ITO in PC is shown in Figure 3. The oxidation wave, with potential for oxidation of 0.76 V vs SCE, corresponds to the phenothiazine (PTZ) moiety. This oxidation process was reversible and maintained a stable color change after 100 successive cycles in $TBAHPF_6$ in PC. The anodic peak current (i_{ap}) showed a linear dependence with a scan rate, v, at small v, with a zero intercept, characteristic of a purely surface electrochemical process. This changed at larger v (over 0.1 V s^{-1}), where i_{ap} varied with $v^{1/2}$, signaling contributions from diffusion control. This behavior is typical of polymer films for electrochemical processes involving fixed or confined redox centers in the polymer film.[28,29] The combined effect of electron transfer (or electron "hopping") between the electroactive groups on the polymer and counterion movement becomes the rate-determining step at higher v (Figure 4).

A comparison of the potential for oxidation of PPTZPQ (0.76 V vs SCE in PC) with that of a phenothiazine moiety (0.67 V vs SCE in benzene/MeCN)[32] shows a

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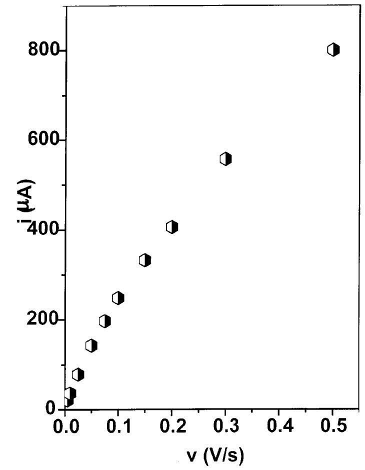

Figure 4. Anodic peak current (i_{ap}) as a function of the scan rate, *v*. PC containing 0.1 M $TBAPF_6$.

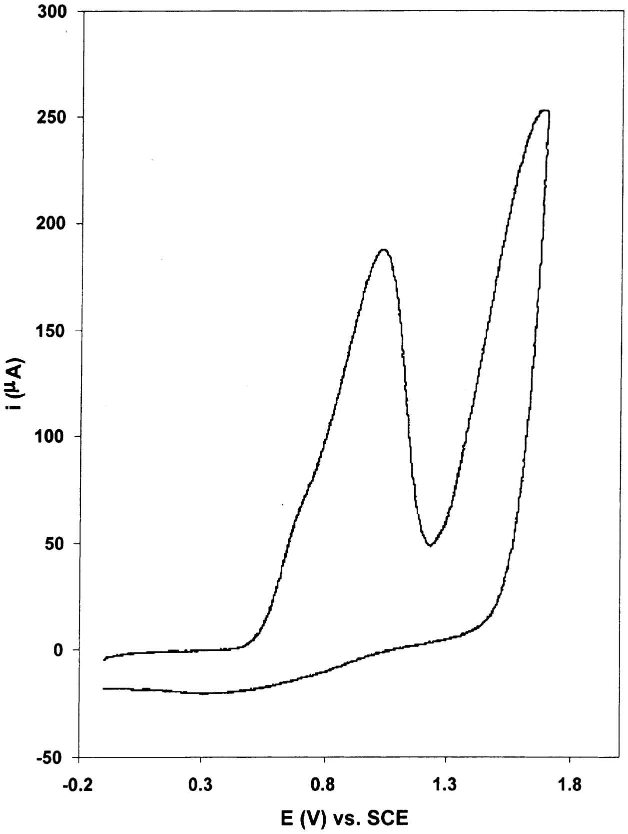

Figure 5. Cyclic voltammetry of oxidation of PPTZPQ film spin-coated over an ITO electrode with PC containing 0.1 M $TBAPF_6$ as the supporting electrolyte. Scan rate 50 mV/s.

difference of 0.09 V. Previous electrochemical and MNDO studies,[32] performed over the repeat unit of PPTZPQ, shows no delocalization of the charge between the phenylquinoline group and the phenothiazine ring upon oxidation and reduction, suggesting that the small shift of the potential to more positive values can be attributed to an inductive effect by the acceptor quinoline moiety on the phenothiazine ring.

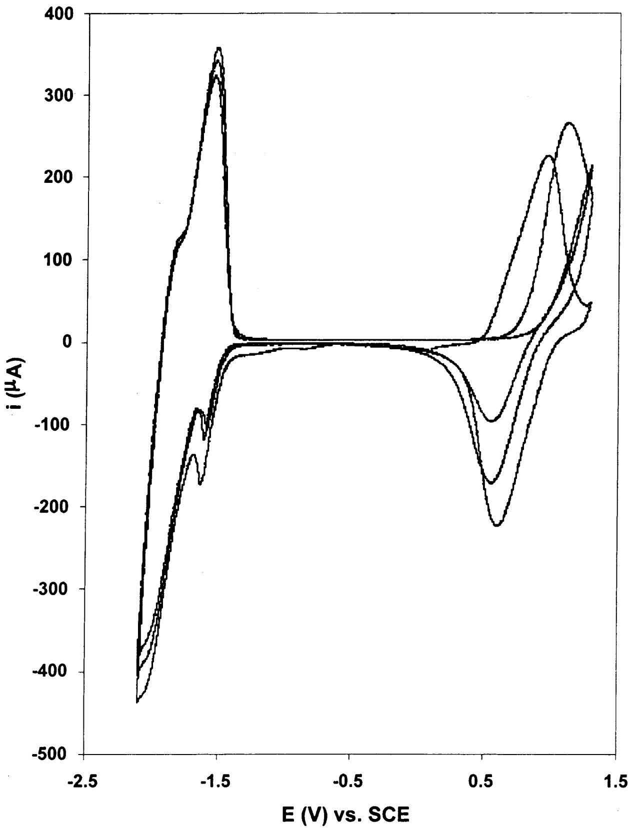

Figure 6. Cyclic voltammetry for the oxidation and reduction of PPTZPQ film spin-coated over an ITO electrode in PC containing 0.1 M $TBAPF_6$ as the supporting electrolyte. Scan rate 50 mV/s.

On the other hand, if the applied potential is positive enough as to produce the highly reactive phenothiazine dication,[30,31] an irreversible wave with a peak potential of 1.68 V vs SCE was obtained (Figure 5). This irreversible chemical reaction produced a permanent loss of the electroactivity and electrochromism of the polymer.

Upon scanning in the negative direction, the cyclic voltammogram showed two fairly well-defined reduction peaks (Figure 6). The reduction waves generated an unstable electrochromic effect, which disappeared after a few cycles. The cathodic process can be assigned to reduction of the phenylquinoline (PQ) group with a peak potential of −2.05 V vs SCE. It is sensitive to the presence of oxygen, and after a few cycles over the range that encompassed the first oxidation and first reduction waves, the anodic electrochromic response was destroyed (Figure 6). This indicates that the quinoline anion radical is participating in a chemical reaction, possibly involving the phenothiazine moiety or its radical cation. Similar behavior was observed in a previous electrochemical study of the dissolved phenothiazine−quinoline monomer.[32]

The observation that the potential for oxidation is not lower than that of the phenothiazine monomer (and is actually a little more positive) suggests that the positive charge in the generated cation radical is not stabilized by delocalization over the polymer backbone. To study the film conductivity and its change with potential, cyclic voltammetry (CV) experiments were carried out with an array of four Pt microbands (1-mm long, 25-μm wide, spaced 25 μm apart).[25,33] CV can be used as a technique to establish if two (or more) microelectrodes

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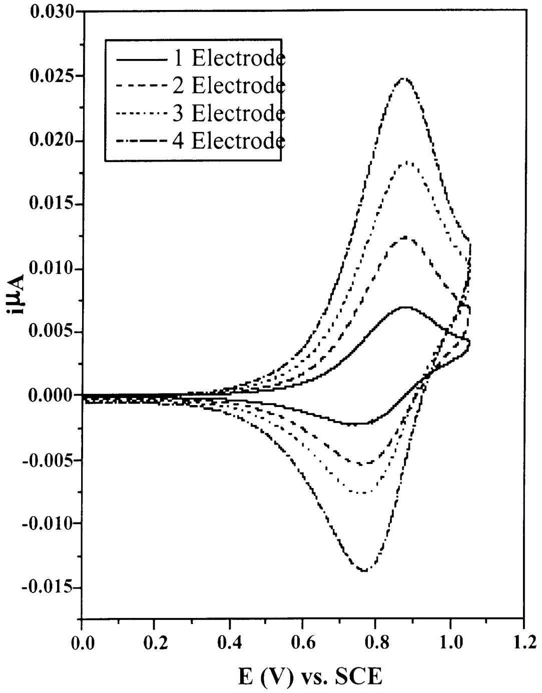

Figure 7. Cyclic voltammetry for the oxidation of PPTZPQ film spin-coated over four Pt microband electrodes in PC containing 0.1 M $TBAPF_6$ as the supporting electrolyte. For one, two, three, and four microbands connected together. Scan rate 10 mV/s.

are electronically connected by the PPTZPQ film. Figure 7 illustrates the data obtained at small v for one, two, three, and four microbands connected together. The voltammograms have different currents or areas, which are proportional to the number of electrodes connected together. In addition, they showed the same current when each electrode was driven, suggesting that the polymer film is homogeneously dispersed over the electrode array. These data indicate that the behavior of each electrode is independent and that the conductivity of the neutral PPTZPQ polymer film is low. In addition, when the two central bands were connected to a voltmeter for a resistance measurement, while the external microbands were connected to the potentiostat, it showed a very small resistance change.

The conductivity was also investigated by SECM. This technique is useful in the study of the transition between insulating and conductive states of electronically conducting polymers.[25,26,34] In general, conductive polymers allow for the regeneration of a mediator species produced at a tip (positive feedback) at the polymer/solution interface, whereas a nonconductive film produces negative feedback, that is, a decrease in the tip current (i_T) as it approaches the film/solution interface. The SECM experiment was carried out by placing a 0.3−0.6-μm PPTZPQ film on an ITO electrode in contact with 1 mM MV^{2+} $TBAPF_6$−PC solution as the mediator, and the tip was biased at −0.6 V. The stationary current obtained far from the sustrate ($i_{T,\infty}$) under these conditions was not constant over the time of the SECM experiment. A possible reason for this behavior is a change in the MV^{2+} concentration due to the low MV^{2+} solubility in PC and perhaps also reaction with oxygen that was not removed from solution. Despite this, the tip current shows a clear positive feedback (the tip-generated MV^+ oxidized back to MV^{2+} on the polymer film) when the film is in the oxidized form and negative feedback when the film is in the neutral form (Figure 8). The negative feedback effect was observed below +0.6 V, where the PPTZPQ is in the neutral form, even when the substrate potentials were sufficiently positive to oxidize the MV^+ to MV^{2+}, indicating that the contribution of the oxidation of MV^+ at the back ITO electrode by diffusion through pinholes in the film was small. Therefore, the positive feedback approach curves are a signal of steady-state conduction of electrons through the PPTZPQ film during oxidation.

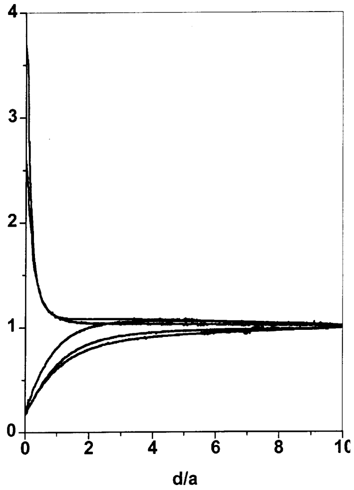

Figure 8. SECM tip (a = 12.5 μm) approach curves with 1 mM MV as the redox mediator on PPTZPQ at different potentials. Potentials are from bottom to top −0.4, 0.0, 0.4, 0.6, and 0.8 V.

In summary, the PPTZPQ polymer film presents a stable anodic electrochemical behavior with color change. In the SECM experiments, PPTZPQ films of 0.3−0.6-μm thickness showed conduction in the oxidized state, but in the four 25-μm separate microbands the observed resistance was high, impeding the quantification of the PPTZPQ film electronic conductivity characteristic.

The charge transport along the PPTZPQ backbone requires the movement of the positive charge to the electron-accepting quinoline moiety, which is an energetically unfavorable process. The conduction of holes through the PPTZPQ film probably occurs by a redox exchange (hopping) mechanism, that is, redox conductivity where the mobile carriers are localized in fixed sites and are transported under force of the concentration gradients by thermally activated hopping or self-exchange between occupied and unoccupied sites.

Film Thickness, Topography, and Permeability. The PPTZPQ film thickness was assessed by surface profilometry and values in the range of 0.2−0.6 μm were obtained. The film thickness (d_f, in μm) was linear with the film absorption at 425 nm (A_{425}) and followed the relation $A_{425} = 4.28d_f$ (Figure 9).

This relation was employed to determine film thickness in the cells and devices.

The PPTZPQ film was imaged by AFM to study the topography of the surface (Figure 10). The image reveals

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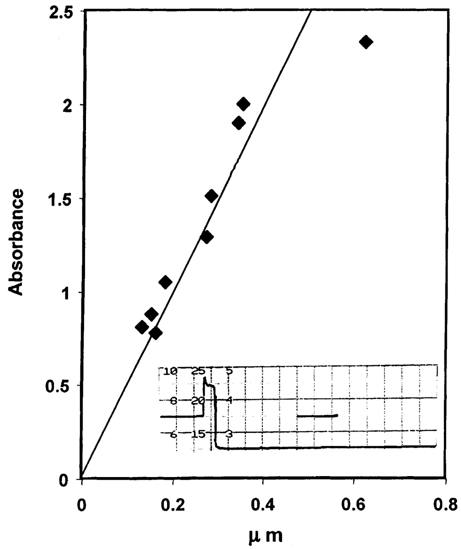

Figure 9. Dependence of the optical absorbance at 425 nm (Ab_{425}) on the PPTZPQ films thickness d_f. Inset surface profile of the edge of a "dry" PPTZPQ film on a glass substrate.

an amorphous structure with a surface roughness of ~300 nm and large depressions. This surface morphology suggests the presence of channels or pinholes in the film. To investigate the film permeability in its neutral form, we performed CV with a mediator in solution over bare ITO and PPTZPQ\ITO.[35] The redox potential of the mediator was chosen within the potential window where the PPTZPQ does not show an electrochemical response and, therefore, behaves solely as a blocking layer on the ITO electrode. If the thickness of the film is of the order of the diameter of the hole, the behavior of the electrode can be treated as an ultramicroelectrode array and the response is determined by the polymer film thickness, size and distribution of the pores, and the time scale of the experiment.[35] The reduction behavior of the MV^{2+} on bare ITO and ITO\PPTZPQ is shown in Figure 11. The smaller current plateau for the coated electrode in comparison with the bare electrode is evidence of a high coverage of the electrode surface with pores spaced far apart in relation to the radius of the pores. The distance between the pores is such that, on the time scale of the experiment, the growth of a diffusion layer for an individual pore does not overlap that of a neighboring pore and produces a decrease in the current proportional to the uncovered area. This result does not indicate the high concentration of pores suggested by the AFM results. The smallest thickness attainable with PPTZPQ was of the order of 0.3 μm. This is thick enough that many of the pores do not extend completely through the film from ITO to solution. This combination of an imaging technique like AFM with the electrochemical analysis represents a useful approach in the study of film permeability.

Spectroelectrochemical Studies. A spectroelectrochemical study of the PPTZPQ polymer film was performed to obtain information about the electronic structure and to examine the spectral changes that occur during redox switching; both of these are important for electrochromic applications. Films, deposited by spin coating on ITO, were immersed in 0.1 M $TBAPF_6$–PC solutions and subjected to potentials over the range of the anodic wave where the films showed stable electrochromic responses. After each potential step, the current in the electrochemical system was allowed to come to equilibrium before taking the optical absorption spectrum. Figure 12 shows the spectra of PPTZPQ as a function of potential between 0.0 and 1.0 V. Neutral PPTZPQ exhibits two absorption peaks, one near 290–300 nm (not shown) and another at 425 nm. The former band can be assigned to a $\pi-\pi^*$ transition in the PQ and the lower energy band, which is less intense, is largely of a charge-transfer character.[22,32] The latter absorption band is responsible for the neutral form of the PPTZPQ film exhibiting absorbance (yellow color) in the visible region. As the potential was increased to positive values, the charge-transfer peak at 425 nm underwent a hypochromic shift concomitant with the growth of new absorption bands. The spectra show two isosbestic points, at 400 and 480 nm (Figure 12). A larger increase in absorption is observed at higher energies (~350 nm) compared to the charge-transfer transition, and a peak at lower energies (540 nm) produces the red color for the oxidized polymer film.

The difference in potential for the oxidation of PTZ (0.67 V vs SCE) and the reduction of PQ (−2.0 V vs SCE) would suggest a charge-transfer transition energy of about 2.7 eV, whereas the energy derived from a 425-nm transition in the spectrum of PPTZPQ is 2.92 eV. This result indicates that in the PPTZPQ polymer there is no marked stabilizing effect of the quinoidal-like forms within the polymer backbone, resulting from a successive zwitterion-like interaction between the A/D units.

The peak at 540 nm, observed at positive potentials, has the same energy as that of the phenothiazine cation radical monomer[32] (which also shows the characteristic red color of the oxidized polymer). The increase in absorption at higher energy could be assigned to the absorption of the PQ and PTZ group.

We can interpret the overall process as follows: the phenothiazine–quinoline (PZT–PQ) repeat unit in the neutral polymer shows charge transfer-type absorption ($PZT-PQ + h\nu \rightarrow PZT^{\bullet+}-PQ^{\bullet-}$) at 425 nm. Following oxidation, the polymer produces phenothiazine radical cation ($PZT^{\bullet+}-PQ$). Charge transfer is no longer possible, and this results in a decrease of absorbance at 425 nm. At the same time, the $PZT^{\bullet+}$ and PQ moieties results in the new peak at 540 nm and the increase in absorption at lower wavelengths (Figure 12).

Electrochromic switching studies were carried out to monitor absorbance change with time during repeated potential steps between the reduced and oxidized states. The PPTZPQ film was switched by stepping the potential between 0 and 0.8 V with switching intervals of 10 s in 0.1 M $TBAPF_6$\PC electrolyte while monitoring the absorbance at 540 nm (Figure 13). The polymer film showed good electrochromic characteristics under aerobic conditions, with a change from the yellow neutral state at 0 V to the red oxidized state at +0.8 V in a repeated and reproducible manner.

PPTZPQ Electrochromic Devices. Thin films of PPTZPQ polymer have stable anodic electrochromic properties, being yellow in their neutral state and red

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(35) Bard, A. J. In *Integrated Chemical Systems*; Wiley: New York, 1994; Chapter 5, p 196.

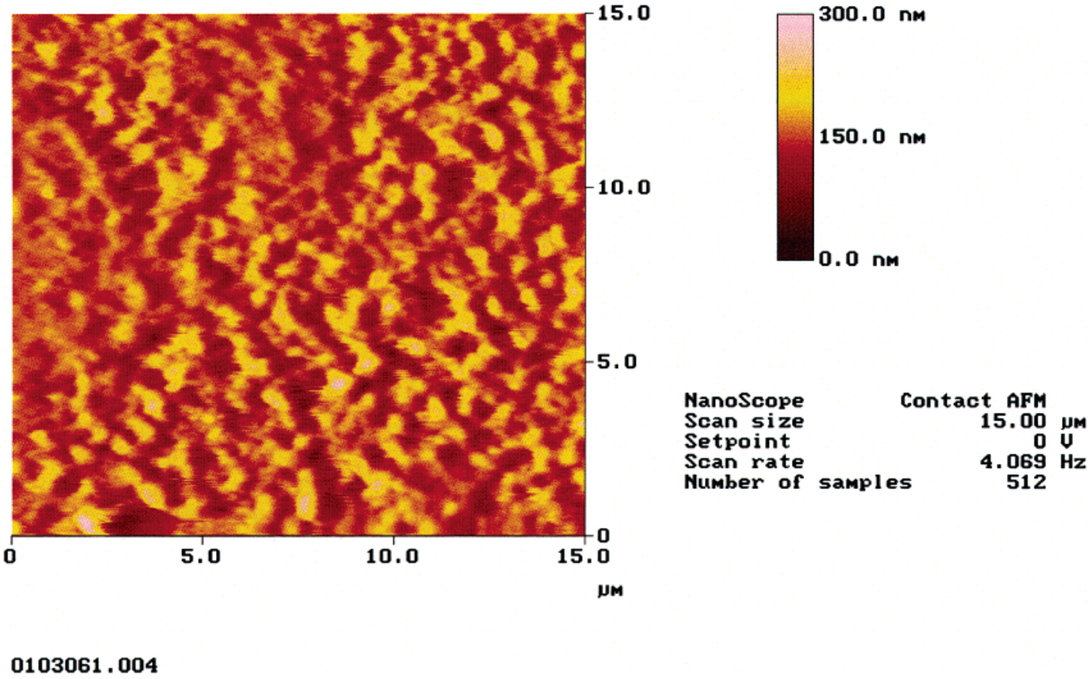

Figure 10. AFM image of PPTZPQ film spin-coated over an ITO electrode.

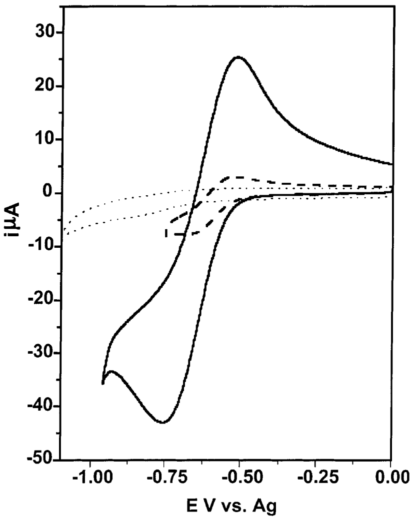

Figure 11. Cyclic voltammograms of 1 mM MV^{2+} in PC, 0.1 M $TBAPF_6$, on a bare ITO electrode (solid line), PPTZPQ-coated ITO electrode without MV^{2+} (dotted line), and PPTZPQ-coated ITO electrode with MV^{2+} (dashed line).

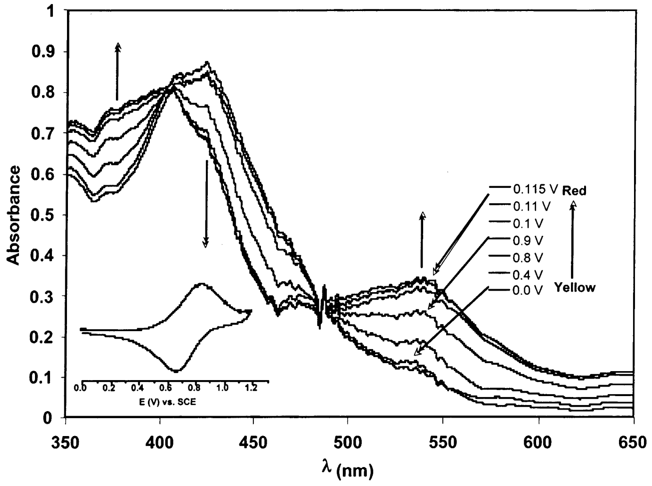

Figure 12. Absorption spectra of PPTZPQ film spin-coated on an ITO electrode at varius applied potentials in PC, 0.1 M $TBAPF_6$. Insets show the potentials at which spectra were obtained.

in their oxidized state, suggesting their use as an electrochromic material. We built and characterized two solid ECDs using PPTZPQ (as the primary electrode) and either BBL or V_2O_5 (as the secondary electrode) deposited over a conducting plastic substrate.

In the construction of a two-electrode cell (Figure 2) with only a single electrochromic material, there may be a problem with degradation reactions of the electrolyte that occur because of the absence of an effective counter electrode reaction. This limits the operating lifetimes through destruction of the electrolyte and a buildup of degradation products in the cell. The use of a reversible electrochromic material as a counter, or secondary, electrode helps avoid this problem. In this way, the electrochemical stability and efficiency of the cell is greatly improved. One approach involves a combination of two electrochromic materials whose neutral state is transparent in the visible spectrum with one electrode anodically colored and the other cathodically colored, allowing the fabrication of a device that

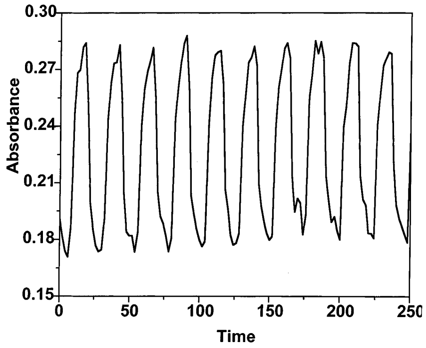

Figure 13. Electrochromic switching, current, and optical response to potential step of PPTZPQ film in PC−$TBAPF_6$ 0.0 and 0.8 V recorded at 540 nm.

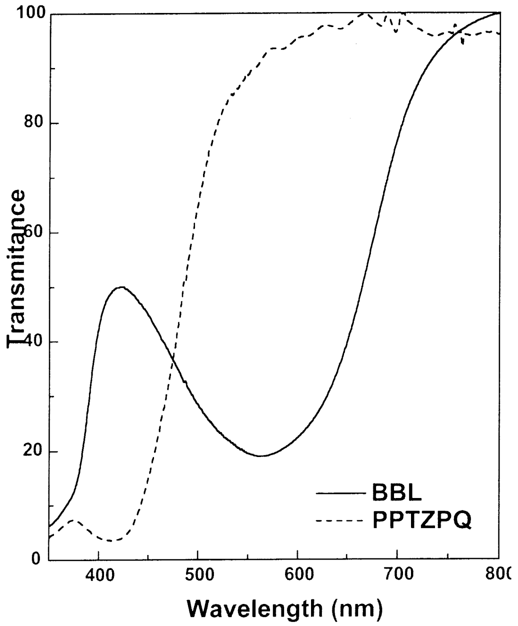

Figure 14. Visible spectrum collected in transmittance mode of PPTZPQ and BBL over ITO film in its neutral colored states.

can switch between highly transmissive and absorptive states, for example, for use as smart windows. In the case of electrochromic materials where the neutral state shows absorption in the visible (like PPTZPQ) spectrum, it is possible to choose as the secondary electrode a material whose neutral state absorption is complementary to that of the primary electrode, and its reduced form shows the same color as that of the oxidized form of the primary electrode. In other words, the combination of the spectra of two complementary colors leads to absorption over the whole visible spectrum, turning the device black. Upon potential switching between the two-redox states, the electrochromic cell will turn from black to the characteristic color of the original forms.

A material that meets these conditions and can be used as a complementary electrode to PPTZPQ is ladder poly(benzobisimidazobenzophenanthroline) (BBL). The spectroelectrochemical properties of BBL have been studied in our laboratory. It is violet (the complementary color of yellow) in the neutral form and is red in the fully reduced state.[25] The spectra of both polymer films are shown in Figure 14. The combination of the two polymer films produces high absorbance over almost the whole visible spectrum and a black color appears when the two neutral films are superimposed. The construction of an all-plastic, two-electrode cell was then successfully accomplished by sandwiching PEO/PC/TBAPF$_6$ as a polymeric electrolyte between films of PPTZPQ and BBL deposited on plastic ITO (Figure 2). The charge capacity of the cathode and anode was equalized ($Q^{PPTZPQ}/Q^{BBL} \sim 1$) by adjusting the film thickness.[36]

The cell was operated within a voltage range where reversible switching was found, without overoxidation of the PPTZPQ or overreduction of the BBL. The application of analysis controlled-potential technique in a two-electrodes cell is limited due to the resulting polarization of the counter electrode. Despite this difficulty, it is possible to obtain useful information, such as the driven voltage and limits of the safe operating voltage by performing cyclic voltammetry measurements. By controlling the total cell voltage to a level just slightly above the difference in standard potentials of both films (the "safe" operating voltage), such operation can be accomplished. In Figure 15 a PPTZPQ−BBL current potential curve is shown, where PPTZPQ was taken as the working electrode. The safe operating applied voltage range was 0.0 to +1.8 V. Within this voltage range the device showed good stability and a black to red color change under anaerobic conditions. When the applied voltage was greater than 1.8 V, the electrochromic response was gradually lost, probably due to formation of some unstable PPTZPQ dication. Degradation was also observed when the device was operated in the presence of oxygen, which reacts with the reduced form of BBL.

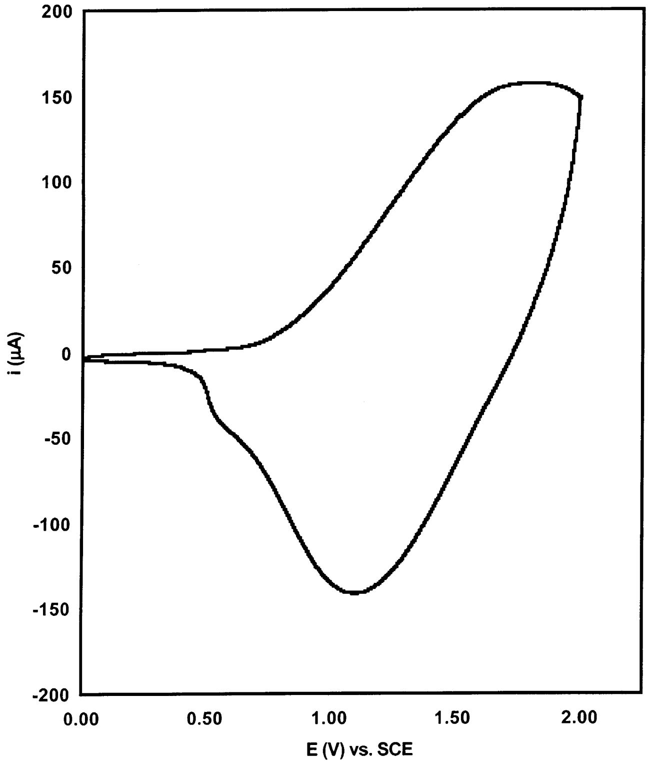

Figure 15. Two-electrode voltammograms for a PPTZPQ/PEO−PC−TBAPF$_6$/BBL cell. Scan rate 50 mV/s.

A second electrochromic cell was fabricated using V_2O_5 film as the secondary electrode and PEO/PC/$LiClO_4$ as the polymeric electrolyte. The V_2O_5 film is yellow and, with the reductive injection of lithium ions into the V_2O_5 film, forms $Li_XV_2O_5$, with a pale blue color. The color changes are rather weak and V_2O_5 films are usually used simply as transparent counter electrodes.[3,7]

Voltammetric studies showed that the PPTZPQ−V_2O_5 cell stably operated with an applied voltage of 0.0−1.5 V under aerobic conditions. Cell testing was carried out by monitoring the absorbance changes at 560 nm as a function of the time during repeated potential steps between 0.0 and 1.5 V (Figure 16). The current transients, in Figure 16, show that the response is slower when the PPTZPQ is oxidized compared to when its cation radical form is reduced. The oxidation current does not reach zero during the 20-s-long potential pulses, whereas the reduction is almost complete within the same time period. However, the amount of charge,

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(36) Chen, L. C.; Ho, K. C. *Electrochim. Acta* **2001**, *46*, 2159.

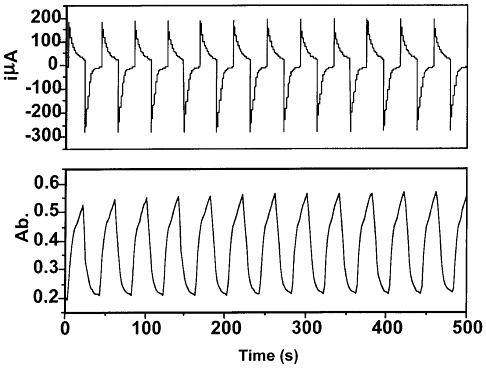

Figure 16. Electrochromic switching, current, and optical response to potential step of a PPTZPQ/PEO−PC−TBAPF$_6$/V$_2$O$_5$ device between 0.0 and 1.5 V recorded at 560 nm.

Q, in each current curve in both processes was very similar, in agreement with the stable oxidation of PPTZPQ and reduction of its oxidized form. The faster reduction can be attributed to an easier charge transport (lower resistance) in the oxidized film. The oxidation of the neutral film starts at the insulating polymer−electrode interface and requires the influx of compensating anions. The reduction process, on the other hand, starts with the polymer in the fully charged state. The kinetics of the overall process is reflected in the coloration response time (Figure 16), which is approximately 20 s.

The coloration efficiency, η, was determined by using the equation[3]

$$\eta = \Delta A(\lambda)/Q_d$$

where Q_d is the injected charge per unit electrode area (C/cm^2) and ΔA is the change in absorbance during a redox step of the device. The absorbance change at 560 nm and under the same potential switching conditions as in Figure 16 yielded a red coloration efficiency, η, of ca. -316 cm^2 C^{-1}. This value is higher than the electrochromic inorganic material WO$_3$. It is also higher than that of electrochromic cells employing polyaniline[17,37,38] and polypyrrole[39] as the anodic coloring material and WO$_3$ as the cathodic coloring material. This value is lower than that obtained for dual electrochromic cells with complementary electrochromic polymers, with total device η-values ranging from 250 to 1413 cm^2 C^{-1}.[20,39,40]

The memory characteristics of the cell, that is, the ability to maintain color at open circuit, were studied by producing the full-oxidized PPTZPQ state and monitoring the cell absorption at 560 nm after disconnecting the power source. The absorption showed a constant (though small) decrease as a function of time (0.01 absorption unit in 1000 s). Both electrochromic cells showed stable operation for hours, but their performance started to decrease irreversibly after a few days of cycling, perhaps because of crystallization of PEO. Although the cell with V$_2$O$_5$ as the counter electrode showed a good lifetime in air, the BBL cell could only be operated for extended periods inside the glovebox.

Conclusions

The electrochemical studies showed that PPTZPQ polymer film undergoes a reversible electrochemical oxidation accompanied by a color change. The reduction behavior of PPTZPQ is unstable and causes loss of the electrochromic effect. The PPTZPQ spectroelectrochemical behavior was interpreted as a combination of the properties of individual donor and acceptor moieties.

The construction of all-plastic PPTZPQ-based electrochromic cells with interesting color changes showed the potential use of PPTZPQ as an electrochromic material as well as flexible all-plastic electrochromic devices. Further work is still necessary to improve the spectroelectrochemical characteristics of these cells by optimizing their charge capacity ratio and particularly the composition of the polymeric electrolyte.

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