These results emphasize the importance of complementing experimental techniques that measure properties averaged over a macroscopic sample with techniques capable of microscale resolution. For example, the scattering and spectroscopic techniques used here were incapable of detecting the TiO_2/VPI-5 sample inhomogeneity observed by TEM and EDX. If the X-ray diffraction peaks in Figure 1b are due solely to scattering from the rodlike regions of the sample, then the influence of occluded titania on the molecular sieve framework stability remains inconclusive. The overall conclusions of this work are significant for those researchers working with supported semiconductor clusters since structure and property measurements of the final system derived from macroscale techniques may be misinterpreted without additional materials characterization on a microscale.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research (ACS-PRF 24446-G5). Suk Bong Hong and James Howe are gratefully acknowledged for their aid with laser Raman spectroscopy and transmission electron microscopy, respectively. Mark Davis is also acknowledged for providing the VPI-5 used in this work.

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New Complementary Electrochromic System Based on Polypyrrole–Prussian Blue Composite, a Benzylviologen Polymer, and Poly(vinylpyrrolidone)/Potassium Sulfate Aqueous Electrolyte

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A new redox complementary electrochromic system is described that is based on electrode surface confined electrochromic polymers. Emphasis is given on the synergism achieved with the implementation of the complementary counter electrode technology: polypyrrole–prussian blue (PP-PB) composite was employed as the oxidatively colored material, and a viologen polymer (pBPQ) derived from *N,N'*-bis[*p*-(trimethoxysilyl)benzyl]-4,4'-bipyridinium dichloride (BPQ) was used as the reductively colored material. A viscous aqueous solution of poly(vinylpyrrolidone) (PVP)/K_2SO_4 was used as the electrolyte. To our knowledge, this is the first example of a complementary electrochromic system where *both* electrochromic materials are electrode surface confined electrochromic polymers. In this paper, the electrochromic materials and the electrolyte are characterized individually, and their properties are discussed in relation to the performance of the electrochromic system. On the basis of the electrochromic system mentioned above, two terminal transmissive and reflective 4 in. × 4 in. electrochromic devices are able to switch from colorless ($A_{400-800} \simeq 0.15$–0.25) to blue ($A_{650} \simeq 1.35$) in about 3–5 s, with the application of 0.8–0.9 V across the two electrodes.

Introduction

Upon oxidation or reduction, certain redox-active materials undergo quite significant changes in their optical absorption spectrum. This phenomenon is called electrochromism, and such materials are called electrochromic.[1,2] Consequently, considerable attention is being focused currently on electrochromism, due to its potential application to light modulation.[1] For this purpose, electrochromic materials are incorporated into electrochromic devices, which are chemical systems composed of one or more such materials and an electrolyte, all confined in a two-electrode electrochemical cell with at least one of its electrodes clearly visible from outside of the cell.

In this paper emphasis is given on surface-confined polymeric electrochromic materials, and the synergism achieved with the implementation of the complementary counterelectrode technology. We report the preparation and characterization of electrode surface confined films of polypyrrole–prussian blue (PP-PB) composite, and we demonstrate functional self-contained reflective and transmissive electrochromic devices incorporating this electrochromic material. A viologen polymer derived from *N,N'*-bis[*p*-(trimethoxysilyl)benzyl]-4,4'-bipyridinium dichloride (BPQ)[3] is employed as the electrochromic material redox complementary to PP-PB, while a viscous aqueous solution of poly(vinylpyrrolidone) (PVP)/K_2SO_4 is incorporated as the electrolyte.

Ideally, an electrochromic device includes two electrochromic materials with "complementary" properties.[4] The first electrochromic material undergoes a colorless-to-colored transition oxidatively, while simultaneously the second electrochromic material undergoes the same color transition reductively. This technology has two distinct advantages. First, the long-term stability of the electrochromic cell is greatly enhanced by preventing any electrolytic decomposition of the electrolyte since both a source and a sink of electrons are provided within the same system simultaneously. Second, the two electrochromic materials change color simultaneously, enhancing the contrast between the colored and colorless states.

Depending on the relative location of the two electrochromic materials within the electrochromic devices, three main types of such devices exist:[4] (a) the solution phase,

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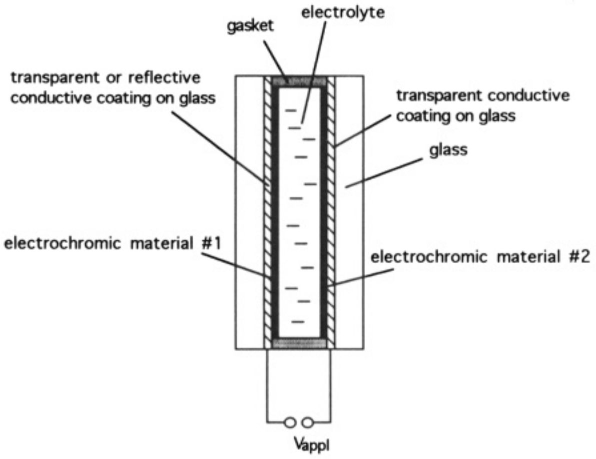
Scheme I. Typical Thin Film Type Electrochromic Device, Based on the Complementary Counter Electrode Technology



(b) the precipitation type, and (c) the thin-film type. In the solution-phase electrochromic devices, the electrochromic materials are dissolved in the electrolyte and they move to the electrodes by diffusion. In the precipitation type, at least one of the electrochromic materials is electroplated reversibly every time the device is cycled between its redox states. Reversible plating of metal ions is a typical example of this category of electrochromic devices.[5,6] Finally, in the thin-film type electrochromic devices, both electrochromic materials are immobilized and confined on the surfaces of the electrodes. Scheme I demonstrates a typical electrochromic device based on such two electrode surface confined thin film electrochromic materials. In principle, surface confinement of both electrochromic materials should provide the highest switching speeds possible, because the redox reaction is expected to change from diffusion controlled to charge transfer controlled. Moreover, physical separation of the two electrochromic materials is expected to prevent annihilation of the colored forms, providing the so-called "memory effect"[1,4] which would significantly decrease the average power consumption. From this point of view, a thin-film type electrochromic device can be considered as a rechargeable battery, in which the color of the electrodes depends upon the state of charge.

The two major classes of electrode surface confined electrochromic materials are certain metal oxides[7,8] and various polymers including conducting polymers.[9] Metal oxides as electrochromic materials switch rather slowly and seem to have problems with their cycling lifetime. On the other hand, conducting polymers do not absorb strongly in their colored states at film thicknesses that would allow one to take advantage of their fast switching speed and strong adhesion to electrodes. Nevertheless, we believe that electrochromic polymers in general are able to accommodate the structural changes induced upon oxidation and reduction easier than other surface-confined materials (e.g., metal oxides), leading to improved cycling lifetimes.

According to the literature, efforts have been initiated to enhance the electrochromic effect of conducting polymers by incorporating into them other electrochromic materials.[10-12] Along these lines, we recently published results on a new class of electrode surface confined electrochromic materials obtained by electroplating the bulk of conducting polymer films, such as polyaniline[13] and poly(3-methylthiophene),[14] with prussian blue. These composites enhance the electrochromic effect of conducting polymers by taking advantage of the strong electrochromism of prussian blue, which can also be reversibly reduced to the colorless Everitt's salt. Importantly, the cycling lifetime of prussian blue seems to be greatly enhanced when incorporated in the polymer matrix, compared with when it is directly deposited on electrodes.[13]

In this paper we characterize polypyrrole–prussian blue composite (PP-PB), which together with a neutral viscous aqueous electrolyte based on PVP is incorporated into complementary electrochromic devices able to switch from colorless to blue. For the reductively colored side of this redox complementary system, the choice is rather limited for surface confined electrochromic polymers. Good candidates, however, are polymers that incorporate the viologen (diquaternized 4,4′-bipyridine) monomer. Individual materials are characterized with emphasis on those properties which are important with respect to the performance of the assembled electrochromic device. To our knowledge, this is the first example of a complementary electrochromic system where both electrochromic materials are electrode surface confined electrochromic polymers.

Experimental Section

Pyrrole, $K_3[Fe(CN)_6]$, $FeCl_3$, K_2SO_4, K_2HPO_4, $NaClO_4$, and anhydrous CH_3CN were purchased from Aldrich. All aqueous solutions were made with deionized (DI) water of resistivity 17.8–18 MΩ cm. *N,N′*-Bis[*p*-(trimethoxysilyl)benzyl]-4,4′-bipyridinium dichloride (BPQ) was prepared by a method described in the literature.[3] Platinum foils were obtained from AESAR and cleaned in a freshly made H_2O_2/H_2SO_4 (1:4, v/v) solution, followed by flame treatment. ITO glass (maximum sheet resistance 5 Ω/sq) was obtained from Metavac, Inc., Flushing, NY, and was cleaned with MICRO cleaning solution. If ITO glass was intended for BPQ deposition, it was also treated with a concentrated KOH solution for ~1 min followed by washing with copious amounts of DI water. All electrochemical depositions and characterizations of the resulting films were done with a PINE RDE4 bipotentiostat. All solutions were degassed with argon, and all potentials were referenced vs a Ag/AgCl reference electrode purchased from Bioanalytical Systems. Polypyrrole was electrodeposited from a 0.2 M solution of pyrrole in 1.0 M $NaClO_4/CH_3CN$, according to well-established literature procedures.[15] Prussian blue was electrodeposited in the polypyrrole film from a 0.5 M aq K_2SO_4 solution containing 5 mM each of $K_3[Fe(CN)_6]$ and $FeCl_3$, by cycling the potential of the polypyrrole covered electrodes from +0.6 to +0.35 V at 50 mV/s until the desired coverage was obtained. A polymer of BPQ (pBPQ) was electrodeposited onto Pt or ITO/glass electrodes by a modification of the literature procedure:[3] the electrodes were typically cycled for 5–6 h at 50 mV/s between 0.0 and −0.75 V in a ~5 mM BPQ solutions in 0.5 M aq K_2SO_4 adjusted at pH ~ 7 with K_2HPO_4.

The electrolyte was prepared by slowly dissolving, under boiling and vigorous stirring, 15 g of poly(vinylpyrrolidone) (PVP; av mol wt 360 000; purchased from Sigma) in 150 mL of distilled water. After dissolution was complete, the solution was concentrated to 100 mL, K_2SO_4 was added so that $[K_2SO_4] \simeq 0.2$ M, and the electrolyte was stored under argon. The viscosity of the electrolyte was measured with a Brookfield Digital Viscometer, Model RVTDV-II, equipped with a small sample adapter. Resistivity measurements of the electrolyte were performed with the ac-

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impedance technique using a PAR 273 potentiostat and a PAR Model 4052 lock-in analyzer, both controlled by PARC M378 software system version 2.50.

Auger surface analysis was conducted, and SEM pictures were obtained with a Physical Electronics Industries Model 590A scanning Auger microprobe spectrometer (SAM). A 10-keV electron beam was used for excitation, and a cylindrical mirror analyzer (CMA) was used for detection. For depth profiling, sputtering was accomplished using a differentially pumped argon ion gun generating a 2-keV, 40 μA/cm^2 Ar$^+$ beam. Samples for Auger were first characterized in both 0.5 M aq K_2SO_4 and CH_3CN/1.0 M $NaClO_4$; they were always disconnected from potential control at +0.5 V vs Ag/AgCl and washed extensively with CH_3CN and H_2O, left in CH_3CN for at least two hours, and subsequently vacuum dried. Brief surface sputtering of the samples prior to analysis to remove impurities was accomplished using a 2-keV, 5.0 nA/cm^2 Ar$^+$ beam.

Electrochromic transmissive devices were assembled using two 4 in. × 4 in. ITO glass plates with $^1/_4$-in. bus bars along all four of their edges. Electrochromic reflective devices were assembled using one 4 in. × 4 in. glass plate sputtered with Cr/Pt, and one 4 in. × 4 in. ITO/glass plate as above. An addressing wire was soldered on to one edge of each plate, and both the bus bar and the solder were insulated. Subsequently, PP-PB or pBPQ were electrodeposited on the plates, as described above. Next, a square viton gasket ($^1/_{32}$-in. thick, obtained from Marco Rubber, North Andover, MA) was attached on top of the bus bar of the pBPQ bearing plate, on the pBPQ/ITO side, and in such a way that when the plate is viewed from the plain glass side, the gasket is completely hidden by the bus bar. Then, the shallow container formed by the gasket and the pBPQ derivatized surface of the ITO glass plate was filled with the electrolyte. Meanwhile, the PP-PB carrying plate was reduced electrochemically to the colorless state of the composite. At this point the electrolyte covered pBPQ plate and the decolorized PP-PB-coated plate were brought together in such a way that no air bubbles were captured in the electrolyte; the excess electrolyte was wiped off, and the devices were sealed.

Spectroelectrochemical experiments were carried out using a PC-controlled Perkin-Elmer Lambda-6 dual-beam UV–vis spectrophotometer. Assembled transmissive devices were placed directly in the light path of the first beam, while two sheets of plain ITO glass were placed in the path of the second beam. Spectroelectrochemical experiments of PP-PB or pBPQ derivatized electrodes were carried out in an argon-degassed and sealed H-cell.

Switching speed determination of 4 in. × 4 in. assembled reflective or transmissive devices was carried out by stepping the potential and simultaneously monitoring both the current and the intensity of the reflected or the transmitted beam, respectively, of a He–Ne laser, using a Si photodiode.

Results and Discussion

(a) On the Oxidatively Colored Side: Polypyrrole–Prussian Blue Composite.

Prussian blue (PB) films on electrodes were first described by Neff[16–18] and Itaya.[19,20] It is known that in solution, Fe^{3+} and $[Fe(CN)_6]^{3-}$ form a one-to-one complex, Fe^{III}–$Fe^{III}(CN)_6$, which seems to be easily reducible at ca. +0.7 V vs SCE.[19] Reduction either of this ferricyanide complex or of Fe^{3+} has been deemed as important steps in the electroplating of PB.[19] PB films in turn, can be reversibly reduced to the colorless Everitt's salt according to[17,19]

$$\underset{\text{prussian blue (PB)}}{Fe_4^{III}[Fe^{II}(CN)_6]_3} + 4e^- + 4K^+ \rightleftharpoons \underset{\text{Everitt's salt (ES)}}{K_4Fe_4^{II}[Fe^{II}(CN)_6]_3} \qquad (1)$$

Due to the significant absorbance change associated with eq 1, PB films have been considered as appropriate for electrochromic[2,21] and photoelectrochromic[22] applications. Clearly, the complementary electrochromic devices we discuss below can also be built with only prussian blue on the oxidative side. However, we have experienced poor cycling lifetime of such films if they are deposited directly on electrodes, and we have reported previously[13] that if PB is impregnated into appropriate polymers such as polyaniline, its cycling lifetime increases dramatically while its electrochromic effect remains unimpaired.

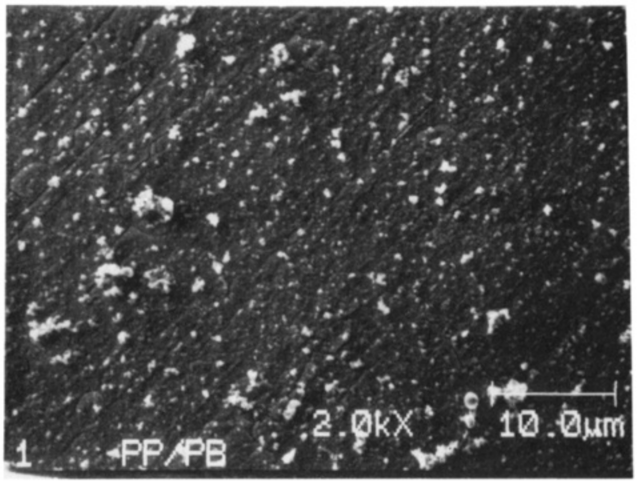

Figure 1. Scanning electron micrograph of a Pt electrode derivatized with PP-PB. $\Gamma_{PP} = 0.81$ mC/cm^2, $\Gamma_{PP\text{-}PB} = 3.34$ mC/cm^2.

In this report, a polypyrrole matrix is impregnated with prussian blue, and the resulting material, together with a viologen polymer, is incorporated into an electrochromic device. Polypyrrole was chosen because of the compatibility of the resulting PP-PB composite films with aqueous neutral solutions (the polyaniline–PB composites are stable only in acidic pHs) and because the PP-PB composite is almost colorless in the reduced state (in contrast, the poly(3-methylthiophene)–PB composite is red[14]). Polypyrrole, like polyaniline and poly(3-methylthiophene),[23] is an insulator when reduced and a fairly good conductor when oxidized above 0.3–0.4 V vs SCE.[24] Prussian blue was then deposited into the polymer layer from a solution containing Fe^{3+} and $[Fe(CN)_6]^{3-}$, by cycling the potential from +0.6 to +0.35 V vs Ag/AgCl. These two ions, either separately, or as a 1:1 neutral complex diffuse inside the polypyrrole film, where they get reduced and plated on the polymer chains. This method of incorporating PB in PP is fundamentally different from previously published electropolymerization of pyrrole in the presence of particles of various inorganic substances[25] including PB.[11] The main advantage of our method is the control it provides with respect to the amount of PB that can be loaded in the polymer.

The SEM picture of a PP-PB composite film (Figure 1) demonstrates a rather smooth surface. The absence of any large aggregation implies that PB has been incorporated into PP in such a way that the resulting material remains microscopically uniform. Auger spectroscopic characterization of the same PP-PB film (Figure 2) verifies that prussian blue is distributed inside the polypyrrole layer,

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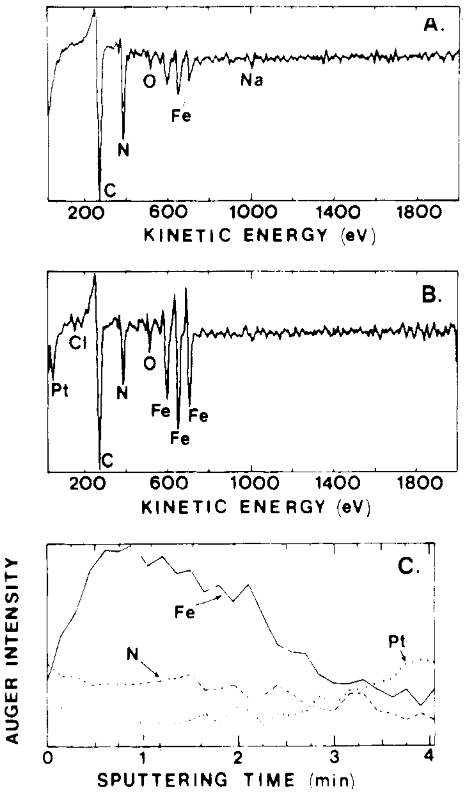

Figure 2. Auger spectroscopic investigation of a Pt/PP-PB electrode. Γ_{PP} = 0.81 mC/cm^2, $\Gamma_{PP\text{-}PB}$ = 3.34 mC/cm^2: (A) initial survey on clean surface; (B) survey during profiling, after 0.7-min sputtering; (C) depth profile, Auger signal intensity as a function of Ar^+ sputtering time.

rather than segregated on the surface. As can be seen in the depth profile presented in Figure 2C, the Fe signal from prussian blue maximizes below the surface of the composite, at a depth that probably reflects the mean diffusion distance of the prussian blue precursors before their reduction to PB. Of course, the morphology of PP which in turn depends on its deposition conditions, together with the concentration of the PB precursors, the potential range, and the scan speed during PB electrodeposition are all important factors that play a role in the distribution profile of PB in PP. The PP-PB films for Auger analysis were first characterized by cyclic voltammetry in both 0.5 M aq K_2SO_4 and in 1.0 M $NaClO_4$/CH_3CN electrolytes, successively, and they were always disconnected from potential control at 0.5 V vs Ag/AgCl to ensure that PB is in the blue oxidized form. The fact that no residual potassium or sodium is seen in the Auger spectra (Figure 2A,B) leads us to conclude that, in agreement with Itaya's results,[19] prussian blue has been deposited in the so-called "insoluble form", that is, $Fe_4[Fe(CN)_6]_3$. Upon reduction it uptakes reversibly K^+ or Na^+ to go to Everitt's salt (see eq 1) or the Everitt's salt analog species $Na_2Fe^{II}[Fe^{II}(CN)_6]$ in non aqueous electrolytes.[26,27]

The cyclic voltammetric characterization of typical PP-PB composite films is shown in Figure 3. The CVs of the composite are dominated by PB, which is to be expected considering the heavy loading of PP with PB. From the scan rate dependence of the anodic peak current shown in inset (a) of Figure 3A and the inset of Figure 3B, we conclude that the oxdation of the composite is faster in CH_3CN/1.0 M $NaClO_4$ electrolyte than it is in aq 0.5 M K_2SO_4. This behavior follows the same pattern as that of prussian blue films deposited directly on electrodes[27] and implies that oxidation of Everitt's salt to prussian blue is still the rate limiting factor for the colorless-to-blue transition of the PP-PB composite films. The fact that in aq K_2SO_4, $i_{p,a}$ vs (scan speed)$^{1/2}$ is linear and passes through the origin implies that a semiinfinite electrochemical charge diffusion condition prevails.[28] However, it should be pointed out that the shape of the cyclic voltammogram in Figure 3A does not exhibit any "diffusional tail". As a matter of fact, the anodic peak current decays faster than it would in a semiinfinite charge

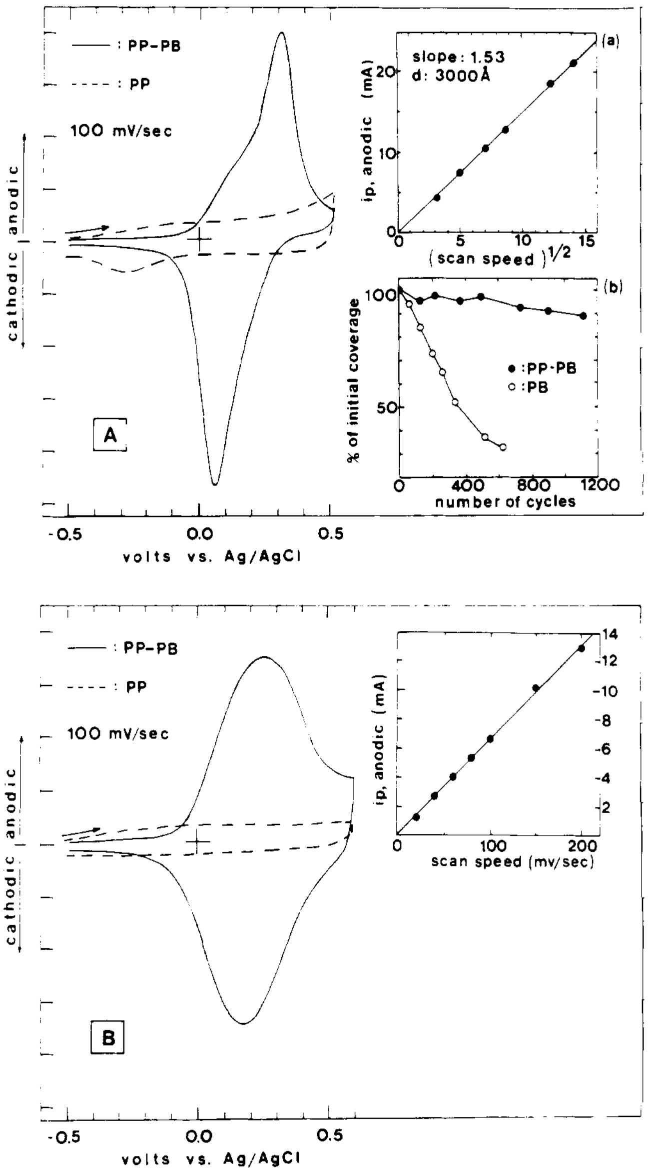

Figure 3. Typical CVs of polypyrrole, before and after loading with prussian blue. (A) In 0.5 M aq K_2SO_4; Γ_{PP} = 0.71 mC/cm^2, current scale 1 mA/division; $\Gamma_{PP\text{-}PB}$ = 7.48 mC/cm^2, current scale 4 mA/division, film thickness (d) $\simeq$ 3,000 Å; inset (a): anodic peak current vs square root of scan speed; inset (b): relative cycling lifetimes of PP-PB vs PB on Pt (Γ_{PP} = 0.76 mC/cm^2; $\Gamma_{PP\text{-}PB}$ = 4.14 mC/cm^2; Γ_{PB} = 4.32 mC/cm^2). (B) In 1.0 M $NaClO_4$/CH_3CN; Γ_{PP} = 0.39 mC/cm^2, $\Gamma_{PP\text{-}PB}$ = 4.22 mC/cm^2, current scale: 2 mA/division; inset: anodic peak current vs scan speed for the same electrode.

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diffusion process.[28] Interestingly, the reduction wave is more symmetric and exhibits an intermediate behavior between equilibrium and semiinfinite diffusion controlled, implying that the reduction of PP-PB to PP-ES is faster than the corresponding oxidation. Nevertheless, due to the strict linearity of $i_{p,a}$ vs (scan speed)$^{1/2}$, we use the Randles–Sevcik equation[29] in order to obtain an estimate of the diffusion coefficient of charge transport (D_{CT}) for the process PP-ES → PP-PB in the film. By this method, D_{CT} is found equal to 1.1×10^{-10} cm^2/s, which is about 1 order of magnitude smaller than the literature value for the process ES → PB in similar electrolytes.[18,22] As will be shown later, an estimated value for D_{CT} allows us to reach certain conclusions regarding factors which limit the switching speed of our devices. Finally, inset (b) of Figure 3A demonstrates that for similar coverages, prussian blue is more durable under redox cycling when it is confined in the polymer matrix than when it is deposited directly on the electrode by itself. The origin of this stability is not well understood. But on the other hand, it is known that the top of the upper valence band of conducting polymers such as polypyrrole[30] and polythiophene[31] resemble that of a linear polyene. Moreover, magnetic studies have shown that in these polymers the heteroatom is not involved in the conduction process, which occurs along the carbon chain.[32] Therefore, it is possible that some of the terminal Fe(III) of the PB lattice coordinate to the nitrogen site of the PP polymer, resulting in better anchored and more durable PB coatings.

(b) On the Reductively Colored Side: Polymer of *N,N′*-Bis[*p*-(trimethoxysilyl)benzyl]-4,4′-bipyridinium Dichloride (BPQ). The most well-known surface-confined electrochromic material for reductive coloration is WO_3.[7] We have not been able, however, to obtain WO_3 films that would survive more than a couple of hundred cycles between the colored and colorless states in neutral aqueous electrolytes. On the other hand, the most well-known non-metal oxide electrochromic materials for reductive coloration have been the viologen (V^{2+}) derivatives,[33] that is, *N,N′*-diquaternized-4,4′-bipyridinium salts. The strong absorbance and the exceptional stability in aqueous solutions of the blue radical $V^{\bullet+}$ obtained from the one-electron reduction of V^{2+} are features very attractive for electrochromic applications. Early efforts to surface confine viologens include *N,N′*-diheptyl-4,4′-bipyridinium dibromide[34-36] that has been used in precipitation type of electrochromic devices and ionene polymers of 4,4′-bipyridine with dihalogenated aromatic or aliphatic bridges.[37] Unfortunately, these polymers cannot develop a chemical bond with the electrode, so that they remain "surface confined" only due to low solubility in the electrolyte employed. In a very interesting effort to increase the stability of electrode coatings of such an ionene polymer of 4,4′-bipyridine with dibromo-*p*-xylene, the polymer was mixed with poly(styrenesulfonate) to form an ion complex.[38]

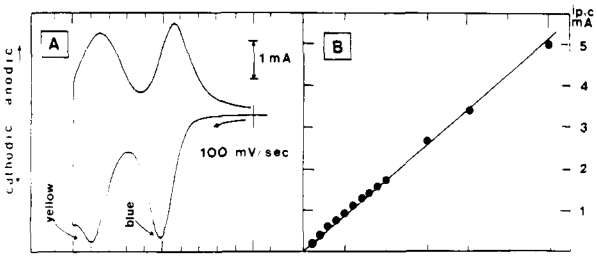
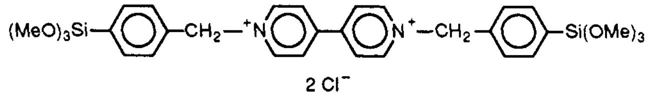


Figure 4. Electrochemical characterization of a pBPQ film on a Pt foil electrode (12.9 cm^2), in an Ar-degassed 0.5 M aq K_2SO_4 solution: (A) cyclic voltammetry, $\Gamma_{pBPQ} = 0.50$ mC/cm^2; (B) scan rate dependence of the first cathodic wave peak current; $\Gamma_{pBPQ} = 0.52$ mC/cm^2.

Eventually, a very successful method of confining viologen on electrode surfaces was developed by Wrighton, who incorporated trimethoxysilyl groups into the basic viologen monomer.[39] One such monomer is BPQ.[3] We



BPQ

were attracted to this material because it has the built-in ability not only to cross-link but also the ability to bind oxidized electrode surfaces through –O–Si–O– bridges. BPQ is reduced electrochemically to the blue $BPQ^{\bullet+}$, which precipitates on the electrode and cross-links via the –Si(OMe)$_3$ functionality to form exceptionally insoluble films. The pBPQ electrodeposition solution we employed was adjusted to pH ~ 7.0, in contrast to the pH ~ 10.0 electrolyte reported in the literature.[3] The reason is that when pH ~ 10.0 electrolyte is used, sections of the polymer film readily breaks and peels off the electrode surface, particularly when the film is rinsed after completion of deposition. Apparently, at pH ~ 10 the pBPQ film forms quickly but with poor adhesion on the electrode. Subsequently, it was found that when deposition solution of about pH 7.0 was used, deposition proceeded slowly, but the resulting pBPQ coatings were extremely robust. Films corresponding to a coverage as high as 2.6 mC/cm^2 have been obtained after 12 h of deposition. It appears that at pH ~ 7.0 polymerization and bonding to the electrode takes place with equal facility.

Figure 4 shows a typical cyclic voltammogram of a pBPQ film in 0.5 M aq K_2SO_4 solution. The first reduction wave gives the blue poly(monocation radical), while the second gives the neutral quinoid species, which is yellow and generally unstable in aqueous solutions.[3,36] The first reduction wave is found to be charge-transfer-controlled (Figure 4B), in agreement with the literature,[3] and quite stable: it survived more than 400 000 cycles at 100 mV/s with a 50% decrease in the charge under the CV; however, its visually perceived ability to modulate reflected light was only minimally impaired.

Figure 5 compares the absorption spectra of pBPQ in the oxidized (dication) and the reduced poly(monocation radical) state in comparison to PP-PB composite in its respective oxidized and reduced states. An extinction coefficient ($\epsilon_\lambda = A_\lambda/\Gamma$) per unit coverage can always be calculated for each film by dividing the absorbance, A_λ, at a certain wavelength λ, over the corresponding film coverage, Γ. Using this surface Beer's law,[28] it is found that

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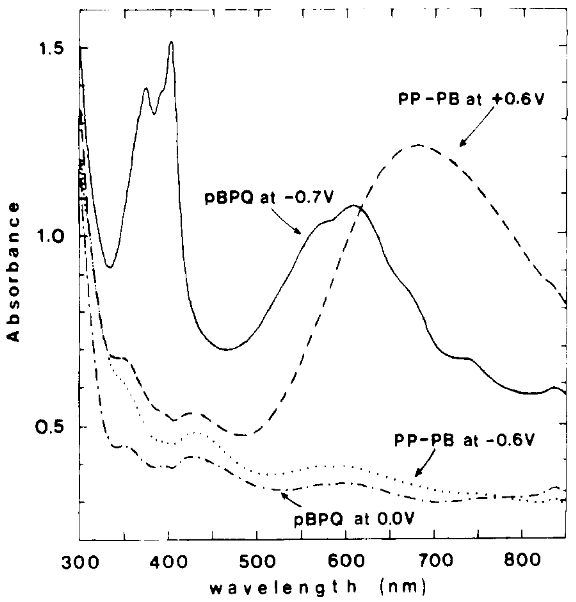

Figure 5. Comparative spectroelectrochemistry of PP-PB and pBPQ in 0.5 M aq K_2SO_4; $\Gamma_{PP\text{-}PB} = 6.95$ mC/cm^2, film thickness $\simeq$ 2800 Å; $\Gamma_{pBPQ} = 1.86$ mC/cm^2, film thickness $\simeq$ 2500 Å.

at the corresponding absorption maxima ($\lambda = \lambda_{max}$) pBPQ absorbs light with $\epsilon_{608} = 0.634$ cm^2/mC, in other words more efficiently than PP-PB, which absorbs light with $\epsilon_{667} = 0.194$ cm^2/mC.

Finally, from Figures 3A, 4, and 5 we can conclude that to force both pBPQ and PP-PB into their blue colored states simultaneously, one has to apply a voltage of 0.8–1.0 V across them. If a voltage larger than 1.2 V were to be applied, pBPQ would be forced into the unstable quinoid form, which should be avoided.

(c) Poly(vinylpyrrolidone)-Based Aqueous Electrolyte. A desirable feature of any electrochromic system is the ability to fit into a variety of applications with little or no modification of its chemistry. For the electrolyte then, desirable properties include nontoxicity and a near neutral pH. On the other hand, practical considerations, such as sealing of the devices, dictates the use of viscous liquids (ideally gels) or solid electrolytes. The reason is that such an electrolyte is also a laminator, in effect "gluing" the two electrodes together.

In this work we employed a 15% (w/v) solution of poly(vinylpyrrolidone) (PVP)[40] in water, with 0.2 M K_2SO_4 as supporting electrolyte. This is a very viscous non thixotropic liquid that behaves as a near newtonian fluid. At room temperature, the absolute viscosity of the electrolyte varies from 1500 cP at 10 rpm to 1340 cP at 100 rpm, while the literature value[41] for the absolute viscosity of 0.2 M aq K_2SO_4 solution at 20 °C is 1.039 cP. The supporting electrolyte contains potassium which is needed for the reduction of prussian blue. Pure PVP is nontoxic and chemically stable[42] and is found to be electrochemically inert. Figure 6A demonstrates that there is a potential window of about 1.5 V available to both Pt and ITO electrodes, where no electrolysis of aq K_2SO_4 either with or without PVP takes place. As mentioned previously, the PP-PB//pBPQ based devices are expected to switch from colorless to blue with a bias of only 0.8–1.0 V; therefore, electrolytic decomposition of the electrolyte should not be a problem. Figure 6B, in turn, demonstrates the ac-impedance response of a cell made of ~1 in. × 1 in. glass/Cr/Pt electrodes and filled with the PVP-based electrolyte. It is found then that at room temperature the resistivity of the PVP based electrolyte is ~36 × 10^3 Ω cm, while the literature value of the corresponding 0.2 M aq K_2SO_4 electrolyte is 28.8 Ω cm at 20 °C.[41] The great difference in resistivity of the 0.2 M aq K_2SO_4 electrolyte with and without PVP, is directly related to the much higher viscosity of the PVP-based electrolyte. Equation 2 employs

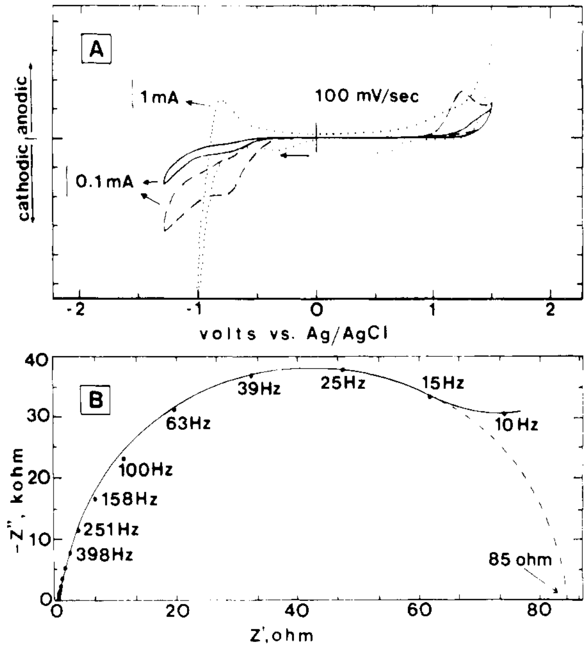

Figure 6. (A) CVs of an ITO (—, 3.4 cm^2), and a Pt (···, 8 cm^2) electrode in 15% (w/v) PVP, 0.2 M aq K_2SO_4 electrolyte; CV of an ITO (– – –, 3.4 cm^2) electrode in aq 0.5 M K_2SO_4 electrolyte. (B) Nyquist plot of a cell made of two glass/Cr/Pt electrodes (area = 5.29 cm^2; thickness = 0.0125 cm) filled with 15% (w/v) PVP, 0.2 M aq K_2SO_4 electrolyte. Dc voltage = 0.0 V; ac voltage = 10 mV.

$$\rho = \left[F \sum_i \frac{z_i^2 e C_i}{6\pi r_i} \right]^{-1} \eta \qquad (2)$$

the well-known Stokes law under terminal velocity in an electric field, substituted into the definition of conductivity,[43] and demonstrates the proportional relationship between the ionic resistivity (ρ) and the viscosity (η) of an electrolyte; z_i, C_i, and r_i are the charge, concentration, and ionic radius of ionic species i in solution, while F is the Faraday constant, and e is the charge of an electron in coulombs. According to eq 2 our resistivity measurements appear internally consistent with our viscosity data: both the resistivity and the viscosity of the PVP-based electrolyte are about 1300 times higher than the corresponding values in the absence of PVP.

(d) PP-PB//Aq K$^+$, PVP Electrolyte//pBPQ Electrochromic System. Two 4 in. × 4 in. electrodes were derivatized the first one with PP-PB and the second one with pBPQ. Subsequently, they were assembled into an electrochromic device (see Scheme I), as described in the Experimental Section. Scheme II summarizes the different coloration/decoloration routes for the PP-PB//K$^+$, aq PVP//pBPQ electrochromic system. Application of a

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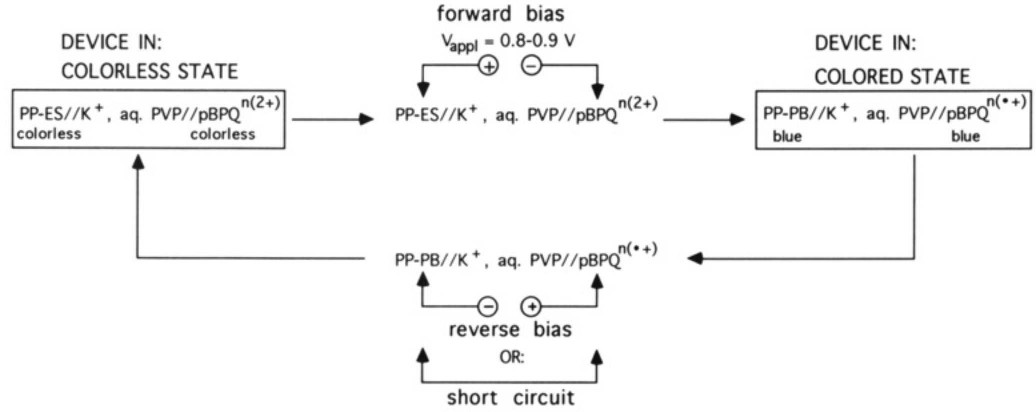
Scheme II. Different Routes of Electrical Addressing of an Electrochromic Device Based on the PP-PB//pBPQ Complementary Electrochromic System



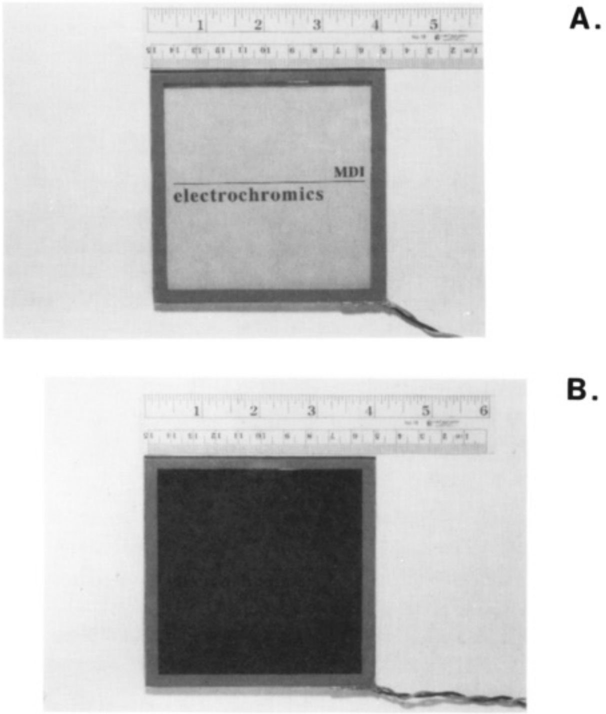


Figure 7. Transmissive electrochromic device employing the chemistry described in Scheme II, placed on top of a white sheet of paper with the letters typed on it. $\Gamma_{\text{PP-PB}} = 6.74$ mC/cm^2 and $\Gamma_{\text{pBPQ}} = 1.81$ mC/cm^2: (A) $V_{\text{appl}} = -0.9$ V; (B) $V_{\text{appl}} = +0.8$ V.

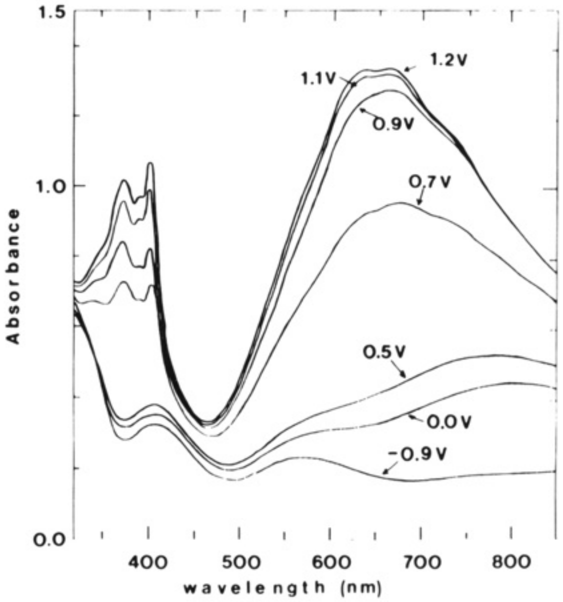


Figure 8. Spectroelectrochemical characterization of the electrochromic device shown in Figure 7. Voltage signs follow the convention of Scheme II.

0.8–0.9-V bias across the two electrodes turns the device from colorless to blue; reversing the bias or simply short circuiting the two electrodes returns the device to the colorless state. Figure 7 demonstrates a picture of such a device. Under either open- or short-circuit conditions, these devices can be stored in the colorless state for months. Similar stability has been observed for the blue state under open-circuit conditions (memory effect). Finally, devices based on the PP-PB//K⁺, aq PVP//pBPQ system have been continuously cycled without any visually noticeable degradation for more than 5000 cycles. However, both the cycling lifetime of such devices and their memory effect depend critically upon the purity of the electrolyte and the exclusion of air pockets from inside the cells. The last requirement probably stems from the well-known fact that viologen radicals reduce oxygen to superoxide which in return couples irreversibly with other viologen radicals.[44]

The absorption spectrum of the device (Figure 7) as a function of the voltage applied across the two electrodes is shown in Figure 8. We observe that both electrodes get colored simultaneously, which is one of the advantages of a complementary system: the absorption spectrum of the entire device consists of the superimposed absorptions of the two individual materials. The voltage required for coloration corresponds approximately to the potential difference (vs Ag/AgCl) between the oxidation wave of PP-PB and the reduction wave of pBPQ, as discussed previously. However, the maximum absorbance of the device is only ~1.35, while the absorbance we would expect if we considered the coverage of both electrodes in relation to the data of Figure 5 should be higher, namely, around 2.5. Obviously, since there is a 3.7 times excess of redox equivalents of PP-PB over pPBQ, the PP-PB composite is only partially oxidized and thus only partially colored when the complementary device is powered with voltage only capable of carrying pBPQ through its first reduction wave. The experimentally measured maximum absorbance of 1.35 for the device of Figure 8 is what one should expect from the ϵ_λ and Γ values of the two electrochromic materials. Nevertheless, devices as shown in Figure 7 and characterized in Figure 8 still absorb ~95% of the light in the region of maximum absorbance. The fact that PP-PB is in redox-equivalent excess over pBPQ implies

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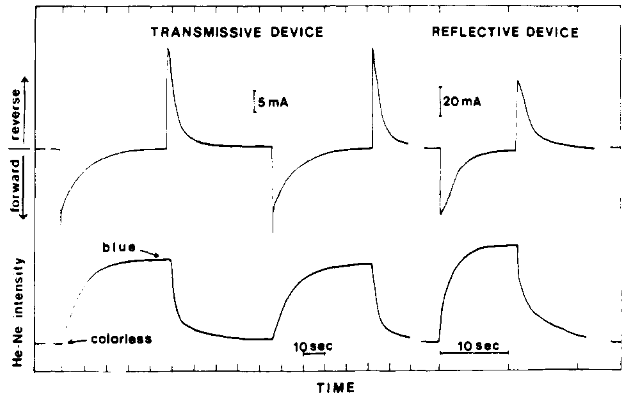

Figure 9. Switching speed determination of a transmissive (both electrodes of ITO), and of a reflective (one Pt, one ITO electrode) electrochromic device. Both devices were 4 in. × 4 in. × $^1/_{32}$ in., and the bias was stepped first from "reverse" 0.9 V to "forward" 0.9 V, and back to "reverse" 0.9 V. Transmissive device: $\Gamma_{PP\text{-}PB}$ = 5.9 mC/cm^2, Γ_{pBPQ} = 2.0 mC/cm^2 (both by CV at 10 mV/sec); charge passed in both directions of potential step: 2.0 mC/cm^2. Reflective device: $\Gamma_{PP\text{-}PB}$ = 5.5 mC/cm^2, Γ_{pBPQ} = 1.9 mC/cm^2 (both by CV at 10 mV/sec); charge passed in both directions of potential step: ~ 1.7 mC/cm^2.

that all pBPQ is able to go to its singly reduced state, and the device appears always blue. If the opposite material balance were true, then colorizing pBPQ fully would force some of the PB into the partially oxidized state known as Berlin green.[21]

Finally, Figure 9 shows typical data obtained for the determination of the switching speed of our prototype electrochromic devices. These data demonstrate that we can control potentiostatically the charging of our devices so that all pBPQ is transformed to the blue poly-cation radical state and that all charge is removable by reversing the bias. Moreover, Figure 9 also shows that a reflective device (one electrode is Pt) switches faster than a transparent device (both electrodes are ITO). These data suggest that a very important switching-speed-limiting factor is the resistance of the electrodes. In fact, if the electrodes were not resistive at all, a 4 in. × 4 in. × $^1/_{32}$ in. device should charge with $\tau = RC \leq 0.1$ s. This value is calculated using 20 μF/cm^2 as a typical double-layer capacitance, and the resistivity of the electrolyte which was found to be ~36 × 10^3 Ω cm. If at this point we use eq 3, we calculate that a ~0.25-μm-thick film of the PP-PB

$$\text{film thickness } (d) = [2D_{CT}\tau]^{1/2} \qquad (3)$$

composite, should get charged in about τ = 3.0 s. Equation 3 is a modification of the root-mean-square displacement formula,[45] which is derived through the Einstein–Smoluchowski random walk theory assuming discrete step size and time units. This equation is useful because it provides approximations of the thickness of a diffusion layer. To use eq 3, we assume a hypothetical diffusion layer equal to our film thickness, where charge diffuses with the D_{CT} value estimated previously, via the Randles–Sevcik equation. However, since the cyclic voltammogram of Figure 3A suggests that the oxidation of PP-ES to PP-PB is faster than simple semiinfinite diffusion controlled, the switching time of 3.0 s is probably a conservative estimate that reflects only the upper limit of that process. On the other hand, a pBPQ film of the same thickness should charge in about 80 ms (D_{CT} for pBPQ is ~4 × 10^{-9} cm^2/s).[3] At this point, the only other factor that limits the switching speed of our devices to longer than 3.0 s is the resistance of the ITO electrode which contributes to the increase of the *RC* time constant of the cell. Nevertheless, the switching speeds demonstrated here compete very favorably even with smaller metal oxide based electrochromic devices reported in the literature.[46–48]

Conclusions

We have demonstrated a complementary electrochromic system based on electrochromic polymers, and a viscous aqueous electrolyte at pH ~ 7. The durability of our materials, together with the color intensity, memory effect, and switching speed of our assembled devices are very satisfactory for practical devices. However, some applications require electrochromic systems with absorbance more uniformly distributed throughout the visible spectrum. Therefore, we plan to introduce electrochromic systems with polymeric electrochromic materials which are not only redox complementary but also complementary in the spectroscopic sense as well. It is known, for instance, that dimethyl-2,7-diazapyrenium salts change from colorless to green upon reduction.[49] 2,7-Diazapyrene is analogous to 4,4′-bipyridine and presumably can be used for surface derivatization via the same –Si(OMe)$_3$ chemistry. Clearly, both redox and spectroscopically complementary electrochromic systems can be built with surface-immobilized 2,7-diazapyrenium salts and conducting polymer–prussian blue composites, in the same fashion as described in this paper.

Another point to note is that the switching of PP-PB composite is faster in certain nonaqueous electrolytes (see insets in Figure 3A,B). This means that PP-PB together with pBPQ and a nonaqueous electrolyte are ideally suited for certain applications, where the refresh rate dictates switching speed requirements.

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