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Polyaniline Exhibiting Stable and Reversible Switching in the Visible Extending into the Near-IR in Aqueous Media

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Spun-cast films comprising polyaniline (PANI) that is template synthesized with poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA, can be reversibly switched between emeraldine salt, leucoemeraldine base, and for the first time, pernigraniline base states in aqueous media at near-neutral pHs. Transitions between the green, transparent and violet states occur within 1−10 s, comparable to the electrochromic switching times reported for thin films deposited via layer-by-layer approaches. Solvent annealing in dichloroacetic acid induces structural rearrangement within PANI-PAAMPSA, resulting in significantly improved stability and reversibility upon repeated cycling, and moreover, imparting tunable polyelectrochromism that extends into the near-infrared (1100 nm).

Introduction

Electrochromic materials comprise redox-active species that exhibit significant, lasting, and reversible changes in color upon the injection or withdrawal of electrons. Electrochemical manipulation of the redox processes in thin layers of these materials thus allows the modulation of the spectral characteristics of light that is transmitted. Upon oxidation, for instance, an electrochromic material can switch from a clear form to a colored form, or vice versa. Electrochromic materials are thus promising candidates in display applications. Devices utilizing electrochromic materials are lauded for their low power consumption because of the passive transmissive mechanism of their operation, as opposed to the active emissive mechanism associated with light emitting diodes (LEDs).[1] Specifically, electrochromic materials require only an initial current pulse at a sufficiently strong potential to induce the desired electrochemical reaction and accompanying chromic change; in the absence of oxidizing or reducing contaminants, this change is permanent and the device only demands backlighting. LEDs, on the other hand, require a constant power supply for continuous photoemission. Additionally, electrochromic devices are easy to fabricate, as the electrochromic materials can be coated directly onto transparent electrodes without the need for the complex patterning that is required for LEDs.[2]

Electrochromism has been reported in redox-active inorganics, such as tungsten oxide;[3,4] small-molecule organics, such as viologen;[5] as well as conducting polymers, such as copolymers and derivatives of polypyrrole and polythiophene.[6,7] Although tungsten oxide was the first electrochromic material of commercial interest, inorganic electrochromic materials typically exhibit slow switching speeds 10−100 s and have proven costly to process because of the need for high-vacuum sputtering deposition.[8] Small-molecule organics, though easy to process, have shown poor stability as they easily diffuse away from the electrode and into the electrolyte. Electrochromic polymers, alternatively, hold the promise of robust film integrity, facile film formability, and fast switching times (< 1 s).[9,10]

Many conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrroles, exhibit an oxidative doping mechanism that can be reversibly accessed via electrochemical processes. Oxidative doping facilitates delocalization of charge carries along the polymer backbone; the electronic excitations that accompany photoabsorption in the doped state occur at larger wavelengths relative to those of undoped species. Oxidative doping thus results in the suppression of $\pi-\pi^*$ transitions

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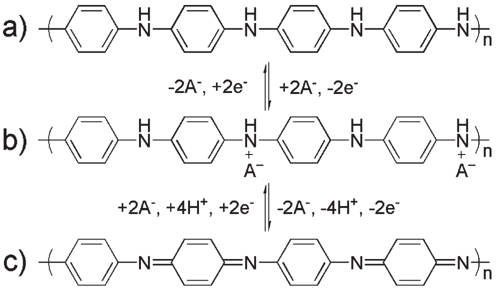

Scheme 1. Reaction Sequence Shows Redox Transitions between (a) LB (fully reduced), (b) ES (intermediate), and (c) PB (fully oxidized), where A^- Represents the Counterion of the Proton Source

in favor of lower energy polaron charge carrier transitions; changes in these transitions can be observed spectroscopically.[11] Given that these transitions typically occur at energy levels within the visible spectrum, many conductive polymers possess intrinsic electrochromicity.[12] PEDOT, for instance, exhibits reversible chromic shifts from dark-blue ($\pi-\pi^*$ absorption near $\lambda = 600$ nm) to visibly transparent (polaron band near $\lambda = 900$ nm) upon oxidation.[13] A vast library of polythiophene- and polypyrrole-based polymers have been synthesized[14-16] and characterized in terms of their electrochromicity.[17,18] Chemically modifying thiophene and pyrrole monomers alters the spectral properties of their polymerized form significantly.[19] In fact, a number of these derivatives even possess multiple oxidation states; switching between these oxidation states results in polyelectrochromic characteristics (i.e., multiple colored states accessible).[10]

Polyaniline (PANI) is another polymer that can exhibit polyelectrochromism. Unlike derivatives and copolymers of polythiophenes and polypyrroles, however, PANI is intrinsically capable of multiple redox transitions (see Scheme 1) without the need for chemical derivatization of the monomer and it thus offers a simple platform for polyelectrochromism.

In its fully reduced form, PANI is known as leucoemeraldine base (LB) and is characteristically transparent ($\lambda_{\max} \approx 330$ nm). In its fully oxidized form, PANI is termed pernigraniline base (PB) and possesses a dark violet color ($\lambda_{\max} \approx 550$ nm). Protonation of PANI's intermediate oxidation state, emeraldine base (EB), results in the formation of the green, electrically conducting emeraldine salt form (ES; $\lambda_{\max} \approx 800$ nm). Preliminary investigations into the polyelectrochromic properties of PANI employed electrochemically polymerized thin films doped with small-molecule acids, such as HCl or H_2SO_4.[20,21] Though capable of stable switching between the green ES form and the transparent LB form on ~1 s time scales and within a ± 1 V potential window in aqueous acidic media (< pH 3), these films lose electroactivity at higher pH as the proton dopants are neutralized and the small-molecule counterions responsible for charge-balancing the doped ES state diffuse away. Moreover, oxidation of PANI to the violet PB extreme in the presence of water results in hydrolytic degradation and loss of electroactivity.[20-22]

Oxidative polymerization of aniline in the presence of polymer acids yields solution-processable PANI complexes.[23,24] Films prepared from these complexes show comparable switching between ES and LB to films that are grown electrochemically. Spun-cast films of PANI complexes, however, exhibit delayed switching times on the order of 100 s, presumably because of slow polymer acid dynamics.[23,25] Alternating the deposition of PANI and polymer acid in a layer-by-layer fashion has generated films capable of switching between ES and LB on the order of 1−10 s. Such layer-by-layer deposition approach, however, is slow (< 20 nm h^{-1}) and necessitates prolonged preparation.[2,9] More importantly, these films also suffer from hydrolytic degradation when subjected to oxidizing potentials so, as with small-molecule acid-doped PANI, access to the violet PB state of PANI has been elusive.[9,22,23,27] To date, switching across the full range of PANI's oxidation states has been demonstrated only in hydrophobic ionic liquids in conjunction with painstaking measures to exclude moisture.[26,27]

Herein, we report and quantify the first demonstration of reversible switching between PANI's LB, ES, and PB states in aqueous media. Unlike systems past, we do not observe hydrolytic degradation at oxidizing potentials, attributed to PANI's enhanced stability at elevated pH when it is template synthesized with poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA.[28] This synthesis yields electrostatically stabilized PANI-PAAMPSA particles that can be dispersed in an aqueous medium and subsequently

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spun-cast to form continuous conductive films over large areas.[29,30] PANI-PAAMPSA films are electroactive beyond acidic pH's; stable and reversible electroactivity extends to pH 9.[28] It follows that transitions to the PB oxidation state can be achieved without chemical degradation or decay in the optical response. The electrochromic response of PANI-PAAMPSA films thus rivals that of films deposited by layer-by-layer approaches while maintaining the processing ease associated with spun-cast materials.

In addition, we show that the optical absorption characteristics of the ES and LB states can be drastically modified by solvent annealing PANI-PAAMPSA films in dichloroacetic acid (DCA). This treatment has been recently reported to enhance the electrical conductivity of PANI-PAAMPSA films by more than 2 orders of magnitude.[31] Extensive structural analysis indicates that DCA moderates the ionic interactions responsible for maintaining PANI-PAAMPSA's globular form and simultaneously plasticizes PAAMPSA, thereby dissolving the PANI-PAAMPSA particles.[31] The conformation resulting from this structural relaxation hastens and stabilizes PANI-PAAMPSA's polyelectrochromic response within the visible region, resulting in switching time scales on the order of 1 s. More strikingly, DCA treatment imparts large and stable NIR transmission contrast, in excess of 50%, between the ES and LB states. This simple post-processing treatment of PANI-PAAMPSA thus extends the spectral range of polyelectrochromism and affords enhanced switching robustness for this readily processable system.

Experimental Section

PANI-PAAMPSA was synthesized as reported by Yoo et al.[32] Aniline (98.9%, Fisher Scientific) was mixed with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA, 10.36 wt % in water, reported $M_w = 800$ kg·mol^{-1}, Polymer Supply, Inc.) at 75 mM in deionized water and deoxygenated under nitrogen. Ammonium peroxydisulfate (APS, 98.9%, Fisher Scientific) was dissolved in deionized water at 100 mM, deoxygenated, and added dropwise until reaching a molar ratio of 0.9:1 APS to aniline. Aniline monomer concentration at the onset of polymerization was 70 mM. The reaction vessel was immersed in an ice bath and stirred for 24 h. After the completion of polymerization, acetone (99.7%, Fisher Scientific) was slowly added to precipitate the PANI-PAAMPSA complex. The resulting product was filtered and dried under dynamic vacuum to yield a green powder that is characteristic of ES. To generate a solution processable dispersion, purified PANI-PAAMPSA was stirred in DI water at 5 wt % for at least 14 days prior to use.

Electrochemical studies were performed at pH 5.0 in 1.0 M acetate buffer solutions comprising sodium acetate (anhydrous, 99.0%, EMD Chemicals) and acetic acid (glacial, 100.0%, Fisher Scientific). The pH of the buffer was verified using an Orion 210 A+ pH meter. All water was purified to 18.2 MΩ using a Milli-Q Academic purification system prior to use. The buffer solutions were deoxygenated for at least 30 min by perfusion of nitrogen gas presaturated with water vapor through a bubbler.

Spectroelectrochemical experiments were carried out in a 1.2 mL cylindrical cell possessing a 1 cm diameter optical port. Spectral characterization was performed on PANI-PAAMPSA films across a UV–vis/NIR spectral range of 190–1100 nm using an Agilent 8453 spectrophotometer with 1 nm resolution. Indium tin oxide (ITO, 15 $\Omega\cdot\square^{-1}$, Colorado Concept Coatings) on glass was used as an optically transparent substrate for spectroelectrochemical measurements; clean ITO samples served as background. Potential step waveforms were generated using a CH-Instruments 660 Electrochemical Workstation. Platinum wire counter electrodes and silver/silver chloride reference electrodes were purchased from CH-Instruments. Silver/silver chloride reference electrodes contained, and were stored in, 3.0 M aqueous potassium chloride (99.0%, EMD Chemicals) solution.

To promote PANI-PAAMPSA adhesion to ITO, bisphosphonic acid (12-phosphonododecyl sulfonic acid, 97%, Sigma Aldrich) was first deposited using the tethering by aggregation and growth (T-BAG) self-assembly method developed by Schwartz et al.,[33] and as previously described.[28] Bisphosphonic acid was dissolved at 0.1 mM in a 95% tetrahydrofuran (THF, distilled in-house to ensure anhydrous and stabilizer free)/5% methanol (anhydrous, 99.8%, Acros Organics) solution. ITO substrates were suspended slightly below the solution-air interface. The solution was allowed to evaporate until no longer in contact with the substrate, in the process depositing the bisphosphonic acid at the air–liquid-substrate interface via condensation reaction between the phosphonic acid groups and ITO's surface hydroxyl groups. The substrates were baked at 130 °C for 24 h following solvent evaporation to drive the condensation reaction to completion. Residual bisphosphonic acid was removed by gently scrubbing the treated substrate with a cotton swab saturated with methanol followed by sonication in methanol. PANI-PAAMPSA was then deposited via spin coating a 5 wt % aqueous dispersion at speeds of 1000 and 5000 rpm and allowed to dry for at least 3 h at ambient conditions, resulting in nominal film thicknesses of 600 and 220 nm, respectively. Films were conditioned by cycling between 0.9 and −0.5 V vs Ag/AgCl in 1.0 M pH 5 acetate buffers solution at 10 mV s^{-1} prior to electrochromic experiments.

To induce structural rearrangement within PANI-PAAMPSA films, we treated samples with dichloroacetic acid (DCA, 99.9%, Fisher Scientific) as described by Yoo et al.[31] After depositing PANI-PAAMPSA on bisphosphonic-acid-modified ITO, films were immersed in DCA at 100 °C and vigorously agitated for approximately 3 min. Excess DCA was removed by blotting the sides of the substrate with tissue; residual DCA was subsequently driven off by heating the film for 30 min at 170 °C.

Results and Discussion

Spectral Influence of DCA treatment. Figure 1 shows the UV–vis/NIR absorption spectra of the three stable oxidation states of PANI-PAAMPSA before and after DCA treatment. The spectra associated with ES were

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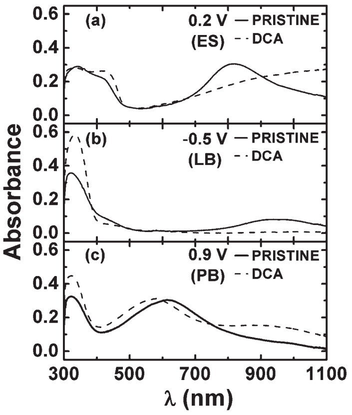

Figure 1. UV−vis/NIR absorption spectra of (a) ES (intermediate), (b) LB (fully reduced), and (c) PB (fully oxidized) forms of PANI-PAAMPSA (—) prior to and (- - -) after DCA treatment.

obtained from 220 nm thick films prior to potential cycling. The spectra associated with LB and PB were obtained from 220 nm thick films at the end of 5 min potential holds at −0.5 and 0.9 V (vs Ag/AgCl), respectively. Comparison between the spectra of the ES states derived from the pristine and DCA treated films reveals stark differences, shown in Figure 1a. Prior to DCA-treatment, the ES spectrum (solid line) exhibits four important characteristics: a peak near 320 nm attributed to aromatic moieties and subsequently referred to as the $\pi-\pi^*$ absorption band; a feature at 420 nm appearing as a shoulder to the $\pi-\pi^*$ absorption and attributed to the polaronic character of the ES state of PANI-PAAMPSA; a large polaron absorption band centered near 800 nm; and a slight free-carrier tail extending off the polaron peak into the NIR region of the spectrum.

After DCA treatment (dashed line; Figure 1a), the polaron shoulder at 420 nm nearly overwhelms the $\pi-\pi^*$ absorption at 320 nm, and the polaron peak, once near 800 nm, is now delocalized into the NIR region. This phenomena has been observed before following solvent annealing of small-molecule acid doped PANI in *m*-cresol,[34] and has been attributed to structural rearrangement of PANI from a compact coil to a more extended conformation.[31]

The LB states of PANI-PAAMPSA derived from pristine and DCA-treated films, illustrated in Figure 1b, also exhibit several differences. The spectrum of pristine PANI-PAAMPSA (solid line) shows absorption bands near 320 and 900 nm and a slight shoulder near 420 nm. The absorption band at 900 nm and the partially retained polaronic shoulder at 420 nm suggest incomplete reduction of the original ES; both features are absent in fully reduced LB.[35] Similar retention of the polaronic character in the LB state was previously associated with PANI having large-molecule counterions,[36] as well as with PANI that is synthesized with polymer-acid templates.[23] We thus attribute this incomplete reduction during the allotted potential hold to mass transfer limitations associated with the high molecular weight polymer counterions.

On the other hand, the UV−vis/NIR spectrum of DCA-treated PANI-PAAMPSA's LB state (dashed line; Figure 1b) exhibits an isolated $\pi-\pi^*$ peak near 320 nm and near-complete transparency beyond 400 nm; the spectrum is in close agreement with previous descriptions of fully reduced PANI.[35] Comparison to the ES spectrum of DCA-treated PANI-PAAMPSA shows that the $\pi-\pi^*$ absorption band grows by almost 100% upon reduction at −0.5 V; the pristine film, alternatively, only exhibits a 25% increase in $\pi-\pi^*$ absorption upon reduction. The 100% increase in absorption at 320 nm is again consistent with previous literature,[35] and suggests that DCA-treated PANI-PAAMPSA undergoes a complete conversion to the LB state within 5 min at −0.5 V. The simultaneous elimination of the polaron peak at 800−900 nm and the polaronic shoulder at 420 nm further support a complete transition from ES to LB in DCA-treated PANI-PAAMPSA. Given that PANI-PAAMPSA adopts a conformationally more favorable structure after DCA-treatment,[31] we speculate that it is this more open conformation of PANI-PAAMPSA that permits rapid and full reduction to LB; conversion from ES to LB is no longer limited by mass transfer limitations of PAAMPSA.

The UV/vis−NIR spectrum of the PB state of pristine PANI-PAAMPSA (solid line; Figure 1c) also exhibits partial retention of ES's polaronic shoulder near 420 nm, as well as a large peak near 630 nm. This large feature is associated with the PB state of PANI, but is red-shifted relative to that expected for fully oxidized PB.[35,37] The presence of a weak polaronic shoulder and the red-shifted position of the PB peak near 630 nm indicate incomplete oxidation of ES, again, likely because of severe mass transfer limitations associated with the polymer acid template.

The UV/vis−NIR spectrum for the PB state of the DCA-treated film (Figure 1c; dashed line) exhibits subtle but important distinctions. Specifically, the polaronic shoulder at 420 nm is completely eliminated upon conversion to PB. Elimination of the polaronic shoulder in DCA-treated films indicates complete departure from the ES form upon oxidation to PB. Comparison between the PB spectra of pristine and DCA-treated films shows that the peak at 630 nm in the former occurs at 580 nm in the latter; a moderate absorption tail extends toward higher wavelengths, but declines near 1000 nm. The appearance of the PB peak at 580 nm, relative to 630 nm for pristine films, is in better agreement with previously reported PB spectra.[38] DCA treatment thus affords a complete transition to PB, whereas the pristine film retains some character of the ES state even after the 5 min potential hold at 0.9 V. Comparison of the UV−vis/NIR spectra in Figure 1 shows that DCA-treated films provide complete access of the full range of PANI's oxidation states,

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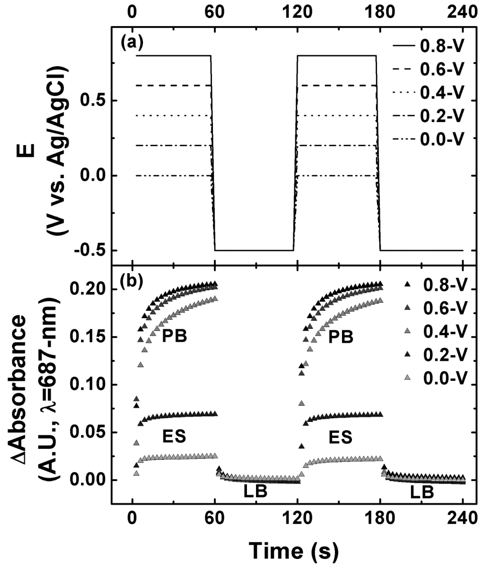

Figure 2. Optical response of PANI-PAAMPSA film on bisphosphonic acid modified ITO as a function of potential in 1.0 M pH 5.0 acetate buffer solution upon switching between ES (intermediate) and LB (fully reduced), as well as between PB (fully oxidized) and LB: (a) applied potential waveform and (b) optical response at $\lambda = 687$ nm as a function of oxidizing threshold.

effectively enhancing the contrast in the visible region and imbuing additional contrast in the NIR region when these films are cycled between ±1 V.

Identification of Optimal Switching Potential. Spectroelectrochemical measurements identified pH 5 to be the highest pH in which distinct PB, ES, and LB states can be readily accessed and clearly resolved.[28] To determine the potential thresholds corresponding to stable LB/ES and LB/PB transitions, 220 nm thick PANI-PAAMPSA films on ITO were subjected to a variety of potential step waveforms.

Figure 2 shows a panel graph illustrating the chromic response of PANI-PAAMPSA to a series of potential step waveforms. Individual potential waveforms are shown in Figure 2a. We started the switching experiments at varying potentials ranging from 0.0 to 0.8 V (vs Ag/AgCl) in 0.2 V increments. After holding at these potentials for 60 s, the potential was switched to −0.5 V vs Ag/AgCl for 60 s to induce transitions to the LB state of PANI-PAAMPSA. As illustrated by the potential waveforms in Figure 2a, the films were cycled again. We used a fresh film during each experiment comprising two 120 s cycles.

Figure 2b shows the optical response of PANI-PAAMPSA to the applied potential. We tracked the absorption changes at 687 nm as the film is subjected to the potential steps. The LB form of PANI-PAAMPSA absorbs very weakly at this wavelength. The high-energy tail of the broad ES polaron absorbs moderately at 687 nm, whereas the PB peak absorbs strongly. Electrochemically cycling between the three oxidation states thus yields large chromic contrast at 687 nm.

The optical response of the PANI-PAAMPSA film cycled between 0.0 and −0.5 V shows a weak but stable modulation in absorption. The response of the film cycled between 0.2 and −0.5 V exhibits absorption modulation that is three times larger than that observed for the previous film. The enhanced modulation arises from the growth and decay of ES's polaron and thus strongly suggests that cycling between 0.2 and −0.5 V induces the film to traverse between ES and LB states, respectively. The UV−vis/NIR spectrum acquired at the end of the potential hold at 0.2 V further confirms the presence of the ES state.[28]

The optical response of the film cycled between 0.4 and −0.5 V shows modulation in absorbance that is yet three times larger than that of the film cycled between 0.2 and −0.5 V. The drastic difference between the two responses suggests that the film now transitions between the PB and LB states during cycling between 0.4 and −0.5 V. Production of PB at 0.4 V is also consistent with previously reported PANI-PAAMPSA electrochemistry,[28] and is again confirmed by the UV−vis/NIR spectrum acquired at the end of the potential hold at 0.4 V. Comparison to the optical response of the films cycled between 0.6 and −0.5 V, as well as that cycled between 0.8 and −0.5 V, reveals similar extents of absorbance modulation, but faster response rates. This observation suggests that switching to PB is most quickly achieved by applying the maximum oxidation potential possible prior to degradation; our previous cyclic voltammetry experiments have identified this extreme to be 0.9 V.[28]

Evaluation of Electrochromic Stability. To investigate the stability and reversibility of the polyelectrochromic switching of PANI-PAAMPSA, a single pristine PANI-PAAMPSA film was subjected to a consecutive series of ES/LB, ES/PB, and PB/LB cycles. In each series, the same 600 nm film was cycled 50 times between the predetermined switching potentials at 120 s per cycle.

Figure 3a shows the optical response of PANI-PAAMPSA upon switching between 0.2 and −0.5 V, corresponding to transitions between ES and LB, respectively. Instead of tracking absorbance, we opted to track changes in transmission for ease in comparison with existing electrochromic literature.[8,18,23] Transmission changes were tracked at the most dynamic wavelength of 784 nm. When in the LB state, the film is nearly transparent and transmits almost 80% of incident light. When the film is oxidized at 0.2 V, transition to ES causes the emergence of the polaron peak near $\lambda = 784$ nm. As a consequence, the film transmits only 50% of the incident light at this oxidation state. The optical response does not plateau during the allotted duration (60 s) for either the oxidation or reduction hold, though both reach 90% of their total change in ~10 s. The ES state exhibits a significant increase in transmission following the first cycle; both the ES and LB states subsequently exhibit slight increases in transmission upon continued switching. Analysis of the UV−vis/NIR response acquired over the entire spectral range (relevant spectra are shown in the Supporting Information) reveals that the increase in transmission at the ES state following the first cycle results from poor recovery of the polaron upon returning from the LB state. Specifically, cycling between LB and ES results in a continual, though slight, decay and

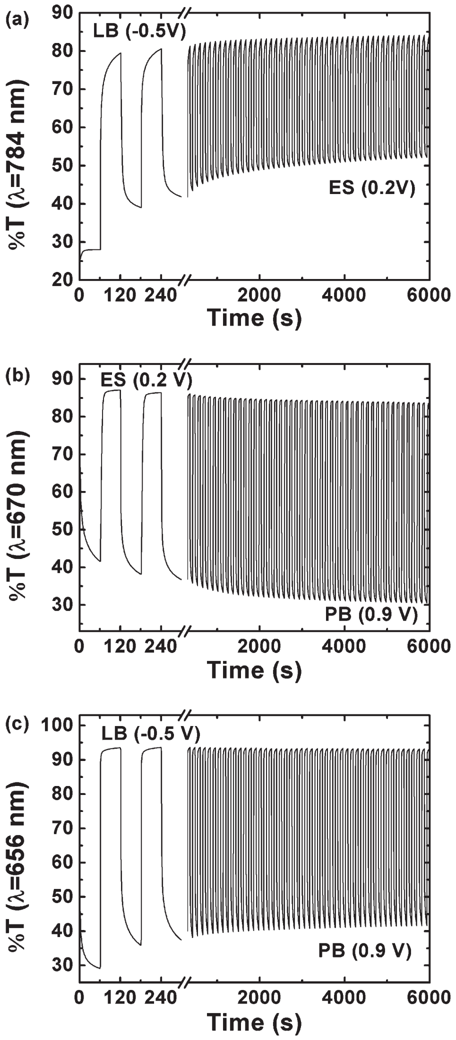

Figure 3. Transmission response of 600 nm thick PANI-PAAMPSA film on bisphosphonic-acid-modified ITO to potential steps. Potential was stepped between (a) 0.2 (ES; intermediate) and −0.5 V (LB; fully reduced), (b) 0.9 (PB; fully oxidized) and 0.20 V, and (c) 0.9 and −0.5 V vs Ag/AgCl for 50 cycles at 120 s per cycle in 1.0 M pH 5 acetate buffer. Maximum optical contrast was recorded at (a) 784, (b) 670, and (c) 656 nm.

red-shift of the polaron peak. Changes in the extent of absorption and the peak position of the polaron suggest continual changes of the polymer conformation, corresponding to different extents of under-oxidation with each cycle. Similarly, we observe an increase in transmission of the LB form with repeated cycling. Phenomenologically, this increase in transmission stems from a gradual suppression of the polaron peak; a manifestation of progressively increasing extents of reduction as the experiment proceeds. We attribute these spectral changes on cycling to slow-occurring structural rearrangements within the PANI-PAAMPSA film. As the film is reduced from ES to LB, the electrostatic interactions between PANI and PAAMPSA that are responsible for maintaining and stabilizing the PANI-PAAMPSA particles are neutralized. The PANI and PAAMPSA chains are subsequently free to sample more favorable conformations, and as a consequence, the particles they comprise gradually relax.[30] Given that this structural relaxation can only occur at the reducing potential where the electrostatic interactions are unlocked, the polymer conformations change progressively each time the film is swung from ES to the reduced state.

Figure 3b shows the optical response of pristine PANI-PAAMPSA upon switching between 0.9 and 0.2 V, corresponding to transitions between PB and ES, respectively. The most dynamic wavelength of the first cycle's spectra was found to be 670 nm. When PANI-PAAMPSA is oxidized at 0.9 V, the PB peak is absorptive at λ = 670 nm and the film transmits less than 40% of the incident light. Upon reduction to ES, the polaron peak shifts to higher wavelengths and the film consequently transmits more than 80% of the incident light at 670 nm. The optical response to oxidation takes nearly 20 s to reach 90% completion. Analysis of UV−vis/NIR spectra taken at the end of the 60 s holds at 0.9 V (provided in the Supporting Information) shows that the broad PB peak progressively blue-shifts and intensifies upon continued cycling. These gradual changes are consistent with the gradually increasing extents of oxidation of pristine PANI-PAAMPSA as the film is swung to 0.9 V each time. We speculate that the same structural rearrangements for which the delayed reduction of ES to LB in pristine films was attributed are responsible for the progressive oxidation of ES to PB with cycling. The electrostatic interactions stabilizing PANI-PAAMPSA are disrupted upon oxidation of PANI, allowing the polymer chains to slowly relax. Accordingly, the gradual decrease in PB's transmittance in Figure 3b reflects the film's optical properties at λ = 670 nm as PANI-PAAMPSA relaxes on cycling. Reduction back to ES takes place in ~1 s, and the film maintains a stable transmittance near 84%. Transitions between ES and PB are very robust; a contrast exceeding 50% is sustained over 100 min of cycling. To the best of our knowledge, these results represent the first report of reversible electrochromic transitions to and from PB state for polymer acid doped PANI.

Figure 3c shows the optical response of PANI-PAAMPSA upon switching between 0.9 and −0.5 V, corresponding to the transition between PB and LB, respectively. The most dynamic region of the first cycle's spectral response was observed at λ = 656 nm. The LB state of the film is highly transparent at 656 nm and transmits more than 90% of the incident light. Upon oxidation at 0.9 V, the polaron peak emerges and blue-shifts toward 656 nm; as a consequence of the strong absorption, the film transmits less than 30% of the incident light at this oxidation state. The transmittance of the PB state during subsequent cycles is higher than that of the first cycle; it subsequently stabilizes near 40% transmittance. When stabilized, the film achieves 90% of its maximum transparency in ~20 s. Transitions to LB occur in less than 1 s and remain stable at 93% transmittance throughout cycling. Similar to the ES/PB transition, switching between LB and PB is very robust and maintains a contrast in excess of 50% after 5 h of continuous cycling. For the first time, the full polyelectrochromic range of PANI can be accessed in a single

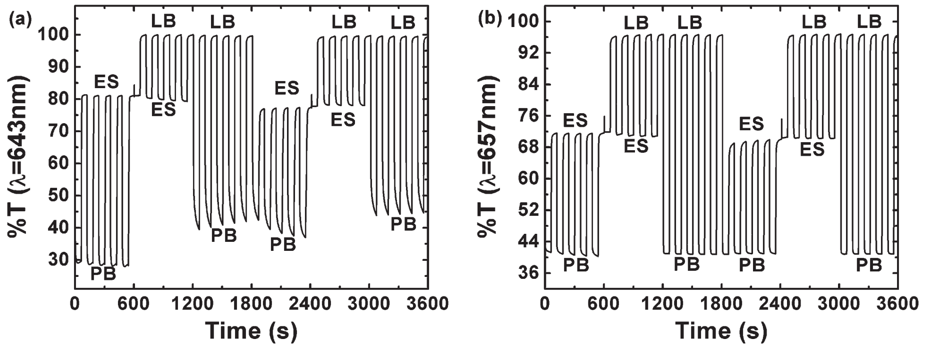

Figure 4. Transmission response of (a) pristine and (b) DCA-treated PANI-PAAMPSA films on bisphosphonic-acid-modified ITO to series of switching potentials. The potential for each set was stepped for 5 cycles at 120 s per cycle in 1.0 M pH 5 acetate buffer solution. Switching thresholds were held at 0.9 (PB; fully oxidized) and 0.2 V (ES; intermediate) for $0 \leq t \leq 600$ s, 0.2 and −0.5 (LB; fully reduced) for $601 \leq t \leq 1200$ s, 0.9 and −0.5 V for $1201 \leq t \leq 1800$ s; this sequence was then repeated for $1801 \leq t \leq 3600$ s. Optical contrast was recorded at local maxima of λ = (a) 643 and (b) 657 nm.

film that is directly spun cast from an aqueous dispersion. Switching between the available chromic states of PANI-PAAMPSA, namely LB/ES, ES/PB, and LB/PB proceeds on time scales comparable to the ES/LB transitions of previously reported polymer-acid-doped PANI systems.[2,9]

Contrast Modification and Enhanced Stability through DCA Treatment. To probe the influence of DCA treatment on the stability and reversibility of polyelectrochromism in PANI-PAAMPSA, we performed a random series of switching cycles on pristine and DCA-treated films. A consecutive series of five ES/PB, ES/LB, and LB/PB cycles were applied to each 600 nm thick film; the series was subsequently repeated to check for hysteresis. The cycles consisted of 60 s holds at the predetermined reduction and oxidation potentials. The maximum spectral contrast throughout the experiment was determined to be at 643 nm for the pristine film. The DCA-treated film exhibited maximum contrast at a comparable wavelength (657 nm), but also offered a large contrast in its transmittance in the NIR centered at 1063 nm. The enhanced contrast at higher wavelengths prompts additional comparison of electrochromic switching in the NIR.

Figure 4 shows the transmission response of (a) pristine and (b) DCA-treated PANI-PAAMPSA films within the visible spectrum at 643 and 657 nm, respectively. Between $t = 0$ and $t = 600$ s, the pristine film exhibits stable switching between ES and PB forms and maintains a contrast near 52%. Switching times are ~5 s. for transitions to PB and below 1 s for transitions to ES. Stable transitions between ES and LB also occur with fast switching times (< 1 s) between $t = 601$ and $t = 1200$ s, though with meager contrast (19%). During $1201 \leq t \leq 1800$ s, however, the pristine film exhibits an increase in transmission in the PB state (39% transmittance) relative to that of the PB state during the initial ES/PB transitions (29% transmittance), and the transmittance further increases upon subsequent cycling. Comparison with Figure 3 attributes this observation to the gradually changing polymer conformation of pristine PANI-PAAMPSA during the first few cycles. Transitions to PB are slow and take nearly 30 s to reach 90% completion. Contrast between the PB and LB oxidation states falls from 60 to 57% within the 5-cycle series. The second series of ES/PB cycles, beginning at $t = 1801$ s, show a gradual decrease in transmittance for the PB state, but fail to completely recover the low transmittances observed in the first series of cycles. The second set of ES/LB cycles is again stable and fast, but the subsequent cycles between LB and PB show further increases in transmission for the PB state of the pristine film.

Between $t = 0$ and 600 s, the DCA-treated film also exhibits stable switching between ES and PB forms, though with suppressed contrast (30%) relative to pristine PANI-PAAMPSA films. Switching times for transitions to PB (~5 s) and ES (< 1 s) are nearly identical to those of pristine PANI-PAAMPSA. Stable switching between the ES and LB states is observed between $t = 601$ and $t = 1200$ s, though the DCA-treated film now exhibits superior contrast (25%) relative to the pristine film. Switching times are < 1 s for transitions to both LB and ES. During $1201 \leq t \leq 1800$ s, the DCA film exhibits fast (< 1 s) and stable transitions between LB and PB forms, quickly reaching the preceding transmission levels observed when switching away from ES. Accordingly, the overall contrast of 55% is a summation of transmittances for the intermediate ES/PB and ES/LB transitions. During the second set of cycles, the DCA-treated film maintains comparable levels of contrast as previously exhibited, and switching occurs at comparable rates. We attribute the enhanced stability of PANI-PAAMPSA's electrochromic response to the preferred conformation arrived at via structural relaxation during DCA treatment. Subsequently unlocking the electrostatic interactions at oxidizing or reducing poles does not confer further conformation changes to PANI-PAAMPSA, so its transmittance is stable and reversible upon repeated cycling.

To probe the viability of NIR switching in pristine and DCA-treated PANI-PAAMPSA, we also compared the stability and rapidity of switching at longer wavelengths. Figure 5a shows the switching characteristics of a pristine PANI-PAAMPSA film at $\lambda = 1063$ nm, the wavelength at which DCA-treated PANI-PAAMPSA exhibits significant contrast when switching between oxidation states. During the first time interval ($0 \leq t \leq 600$ s), the pristine film stably transitions between the ES and PB states, and exhibits a contrast of 19% between the two states.

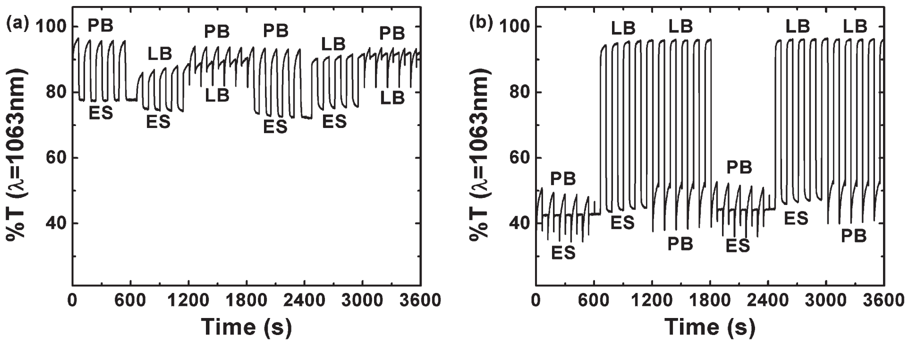

Figure 5. Transmission response of (a) pristine and (b) DCA-treated PANI-PAAMPSA films on bisphosphonic-acid-modified ITO to series of switching potentials. The potential for each set was stepped for 5 cycles at 120 s per cycle in 1.0 M pH 5 acetate buffer solution. Switching thresholds were held at 0.9 (PB; fully oxidized) and 0.2 V (ES; intermediate) for $0 \leq t \leq 600$ s, 0.2 and −0.5 (LB; fully reduced) for $601 \leq t \leq 1200$ s, 0.9 and −0.5 V for $1201 \leq t \leq 1800$ s; this sequence was then repeated for $1801 \leq t \leq 3600$ s. Optical contrast was recorded at $\lambda = 1063$ nm.

Switching to ES occurs in less than 1 s, but transitions to PB take in excess of 10 s. Contrast between ES and LB becomes progressively smaller for $601 \leq t \leq 1200$ s, as the film becomes increasingly transparent in the LB state. The ES/LB transition exhibits an average contrast of 12%; switching to the ES state occurs in less than one second, though transitions to the LB state proceed on 20−30 s. time scales. Between $t = 1201$ and $t = 1800$ s, the pristine film is switched between the LB and PB states. Contrast between these two states is meager (3%), while switching times are on the order of 20−30 s. for both transitions. As with the ES/LB series, transmittance in the LB state continues to increase throughout the cycle, leading to progressively less contrast between the two oxidation states. Comparison to the initial ES/PB series, alternatively, shows that the transmittance in the PB state has dropped by ~4%. Significant hysteresis is observed throughout the second set of cycles. The second round of ES/PB transitions exhibits similar switching times and contrast to the first set, but the transmittance of each state has dropped by nearly 5%. The second series of ES/LB cycles exhibits a slightly improved contrast of 15% relative to the first series, but the switching time associated with the transition to ES has increased to ~15 s. The transmittance associated with the LB state continues to increase upon repeated cycling, leading to decreasing contrast. The final LB/PB series exhibits a contrast of only 2% and switching times in excess of 20 s. for each transition.

The polyelectrochromic behavior of pristine PANI-PAAMPSA in the NIR region provides poor contrast, slow switching speeds, and the transmittance appears to be history dependent. The DCA-treated film, however, exhibits high contrast, fast switching speeds, and stable polyelectrochromism in the NIR region. Figure 5b shows the optical response of DCA-treated PANI-PAAMPSA at 1063 nm. Transitions between ES and PB occur for $0 \leq t \leq 600$ s. Although transitions to ES occur in less than 1 s, switching times of 20−30 s are associated with transitions to PB; contrast is limited to 5%. The truly remarkable behavior of DCA-treated PANI-PAAMPSA is revealed upon cycling between LB and ES. For $601 \leq t \leq 1200$ s, the LB/ES transition offers large and stable contrast (50%), and switching times below 5 s. Between $t = 1201$ and $t = 1800$ s., the film is cycled between PB and LB. Transmittance in the PB state is slightly higher than for the ES state; as a consequence, the contrast for PB/LB switching drops to ~45%. Transitions to the LB state occur below 5 s, whereas transitions to PB exceed 30 s. The second series of cycles maintain similar contrast and switching times to those exhibited in the first set, though with slight transmittance increases in the ES state. The switching behavior of the DCA-treated film in the NIR region maintains a contrast near 50% after an hour of cycling. These results indicate a dramatic performance improvement over pristine PANI-PAAMPSA films in the visible spectral range extending into the NIR in terms of contrast, switching times, and stability.

Conclusion

PANI produced through template polymerization with PAAMPSA exhibits transitions between the transparent reduced LB state, the green intermediate ES state, and the violet and oxidized PB state, all within a potential window of −0.5 to 0.9 V (vs Ag/AgCl). To the best of our knowledge, this is the first report of stable switching to PB, and hence polyelectrochromism, of PANI in aqueous media. Furthermore, solvent annealing of PANI-PAAMPSA films with DCA drastically modifies the spectral properties of PANI-PAAMPSA, providing enhanced absorption extending well into the NIR spectrum. The structural rearrangement attributed to DCA treatment allows quick and complete access to the fully oxidized and reduced forms of PANI.

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Supporting Information Available: Intermediate spectra obtained during various polyelectrochromic transitions are shown and discussed (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.