

Black-to-Transmissive Electrochromism with Visible-to-Near-Infrared Switching of a Co(II)-Based Metallo-Supramolecular Polymer for Smart Window and Digital Signage Applications

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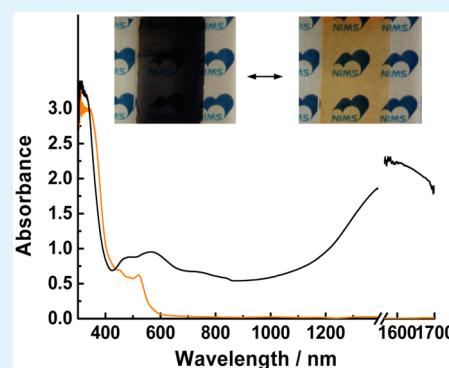
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S Supporting Information

ABSTRACT: Black-to-transmissive electrochromism has been obtained with a Co(II)-based metallo-supramolecular polymer (polyCo). Thin films of polyCo, based on bisterpyridine ligand assembled with Co(II) metal ion, were constructed by spray casting the polymer onto ITO glass. With such simple fabricating means to form good-quality films, polyCo films show stable switching at the central metal ion of the Co(II)/Co(I) redox reaction when immersed in aqueous solution. With an increase in the pH of the aqueous electrolyte solution from neutral, the film exhibits a color response due to the interaction between the d-orbital electron and hydroxide ions affecting the d–d* transition. As a result, a nearly transparent-to-black electrochromic performance can be achieved with a transmittance difference at 550 nm of 74.3% (81.9–7.6%) in pH 13 solution. The light absorption of the film can be tuned over light regions from visible to near-infrared with a large attenuation.

KEYWORDS: aqueous, bisterpyridine, cobalt, electrochromism, metallo-supramolecular polymer



INTRODUCTION

The word “electrochromism” originates from a paper by Platt published in 1961 that defined the phenomenon of an electroactive material undergoing an optical spectrum change upon an electron transfer reaction induced by the application of an external bias.¹ Electrochromic materials can exhibit absorption changes in the ultraviolet (UV; 190–380 nm), visible (vis; 380–780 nm), and near-infrared (NIR; 780–2000 nm) light regions. In addition to applications in smart window, antiglazing mirror, digital signage, and electronic paper, electrochromics are also exploitable in thermal control, optical communications, and data storage.² Numerous materials have been investigated for these functions,³ including inorganic materials such as metal oxides and transition metal complexes as well as organic materials such as organic molecules and conjugated polymers. Recently, a new class of inorganic–organic hybrid materials, metallo-supramolecular polymers, has been developed, and these hold promise for electrochromism. On the basis of the construction of metal ions linked with organic bridging ligands, this type of material has attracted increasing interest owing to their tunable composition at the molecular scale.^{4–9} The characteristics of metal-to-ligand charge transfer (MLCT) and intervalence charge transfer (IVCT) enable these hybrid materials to exhibit visible and NIR electrochromism.^{10,11}

Our recent research on metallo-supramolecular polymers has shown various electrochromic performance with respect to

different metal ions and ligands.¹² Metal ions, e.g., Ru, Fe, Co, Cu, Ni, and other transition metals, have proved to play a key role in the color variation of these polymers based on the d–d* transition or MLCT absorption.^{13,14} The solvent dependences of the intramolecular electronic distributions of several kinds of metal–ligand complexes have also been well examined.¹⁵ Properties of metal ions may be altered with different solvents of different polarities, solvating abilities, etc.^{16,17} Our past investigations of metallo-supramolecular polymers mostly showed a stable color change in an organic solvent electrolyte. Among the metal ions that act as redox centers, Co ion is known to have unique properties with water molecules. Co(II) is likely to form a hexaaqua complex, Co(H₂O)₆²⁺, in aqueous solution, and thus, a mixed-ligand complex with strongly coordinating solvent molecules was speculated to give rise to the electrocatalytic property.^{18–20} Co(I) complexes also exhibit interesting chemistry as an excellent catalyst of hydrogen production from water since it is a powerful nucleophile.^{21,22} Moreover, mixed-valence Co(II)/Co(I) supramolecular complexes have been found to be stable in an aqueous environment.²³ According to the Robin–Day classification,²⁴ the Co(II)/Co(I) complex corresponds to a class II–III mixed-valence species,²⁵ leading to possible NIR absorption.

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In this work, we demonstrate the electrochromic performance of a Co(II)–bisterpyridine metallo-supramolecular polymer film (polyCo, Figure 1) that switches in aqueous

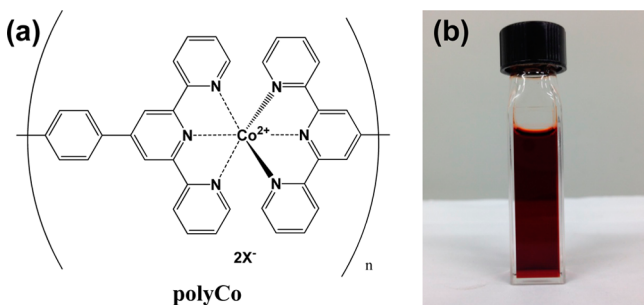


Figure 1. (a) Molecular structure and (b) MeOH solution (4 mg mL⁻¹) of the polyCo polymer. For as-prepared polyCo films, the counterion X⁻ is OAc⁻ and is replaced by Cl⁻ after redox switching in KCl solution.

electrolyte solutions. With the reduction of the metal center from Co(II) to Co(I), the polymer thin film exhibits a stable deep black color that switches in an electrolyte solution of water rather than an organic solvent. Increasing the pH of the aqueous solution results in the thin film displaying further bleaching in the oxidized state. As a consequence, the polyCo thin film exhibits black-to-transmissive electrochromism over a wide attenuation range of 300–1700 nm. To the best of our knowledge, the optical contrast based on the *L**, *a**, and *b** colorimetric index is superior to the values of previously reported black electrochromic materials.^{26–30}

EXPERIMENTAL METHODS

Cobalt(II) acetate (Co(OAc)₂) and sodium hydroxide (NaOH) were purchased from Wako Chemicals. 4',4''-(1,4-Phenylene)bis(2,2':6',2''-terpyridine) (ligand, 97%) and potassium chloride (KCl) were purchased from Aldrich. All chemicals were analytical grade or better and used as received. All solutions were prepared with ultrapure water (18 MΩ cm) throughout the experiments, except methanol (MeOH, Wako Chemicals), which was dehydrated using molecular sieves and used during the synthesis of the polymer. The preparation of polyCo polymer was achieved according to our previous procedure.¹³ An equimolar amount of the ligand and Co(OAc)₂ was refluxed in MeOH under argon atmosphere for 24 h. The resulting solution was cooled to room temperature and filtered to remove a small amount of insoluble residues. The filtrate was slowly evaporated to remove the solvent, and the product was collected and dried further in vacuum overnight to give the corresponding polyCo polymer (>90%). The molecular weight (*M_w*) of polyCo was determined to be 4.31 × 10³ using gel permeation chromatography (GPC) (Instrument LC-9110 NEXT, JAI; column JAIGEL-3HAF+4HAF; eluent 100 mM LiBr in DMF; flow rate 1.0 mL/min; detector UV-370 NEXT@268 nm; injection volume 0.1 mL; standard polystyrene). The polymer was dissolved in MeOH of 4 mg mL⁻¹ before use (Figure 1b). It is noted that at high concentration of the casting solution, the polymers prefer to aggregate due to the strong ionic interaction between metal-polymer chains. Once the polymer film formed, it shows high stability to water and strong treatment such as ultrasonication is necessary to dissolve the film.

All polyCo thin films were prepared using a spray-coating method by casting the polymer solution onto an indium tin oxide (ITO) glass with a mask to confine the active area to 1 × 3 cm². The film is homogeneous and smooth as shown in Figure S4(a). The film thickness was measured to be approximately 800 nm using a scanning electron microscope (SEM, Hitachi S-4800) as shown in Figure S1. The polymer film/ITO was immersed in water for examination, and

no polymer dissolution was observed after continuous immersion for more than 30 days. All electrochemical experiments including cyclic voltammetric (CV) and amperometric measurements were carried out on an ALS/CHI model 612B electrochemical workstation (CH Instruments, Inc.). A conventional three-electrode system was used with the polyCo-coated ITO glass as the working electrode, platinum wire as the counter electrode, and Ag/AgCl/saturated KCl (BAS Inc., Japan) as the reference electrode. All potentials reported in this work are against the Ag/AgCl/satd KCl reference electrode. UV–vis–NIR spectra were recorded using a Shimadzu UV-3600 spectrophotometer. Colorimetric measurements were carried out using a Shimadzu UV-2550 UV–vis spectrophotometer for the index of lightness (*L**) and color coordinates (*a**, *b**) according to the Commission Internationale de l'Éclairage 1976 *L* a* b** model. The pH of the KCl electrolyte solution was modified by the addition of HCl or NaOH and determined by a HORIBA F-52 pH meter. All experiments were performed at room temperature.

RESULTS AND DISCUSSION

A polyCo film (absorption at 520 nm = 0.62 au) cast on ITO glass was cycled between 0 and –1.3 V in 0.1 M KCl_(aq) for steady redox switching before measurement of the absorbance spectra. The initial cycling of redox-active films commonly shows structural changes in the material;³¹ however, there was no obvious change in the CV shape upon initial cycling of the polyCo film (Figure S2). Therefore, 10 cycles of the as-prepared film were scanned, and this was considered as reaching the steady state. As shown in Figure 2, the bleached

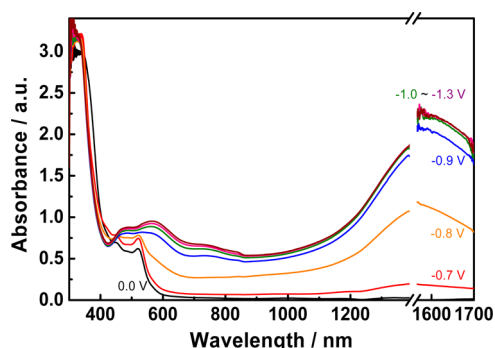
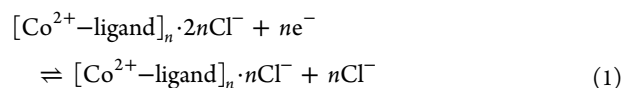


Figure 2. In situ UV–vis–NIR absorbance spectral change of a polyCo film spray cast on ITO glass at applied potentials from 0 to –1.3 V in 0.1 M KCl_(aq). Absorption data at wavelengths ranging from 1395 to 1555 nm have been removed for clarity because of the interference of water molecules.

film at 0.0 V displays the distinct d–d* transition band of Co(II) in the visible light region around 520 nm.¹³ The absorption peak at around 340 nm represents intraligand charge transfer (or π–π* transition), of which the intensity remains nearly the same as the potential is changed. When a reduction potential more negative than –0.7 V is applied to the film, simultaneous darkening until –1.3 V is observed, consequently resulting in broad-band absorption covering the visible to NIR light regions. With the corresponding electrochemical behavior characterized through cyclic voltammetry (Figure 3), this electrochromic reaction is assigned to the reduction of the metal ion from Co(II) to Co(I).^{18,32,33} Accordingly, the reaction of polyCo switched in KCl aqueous solution can be described as



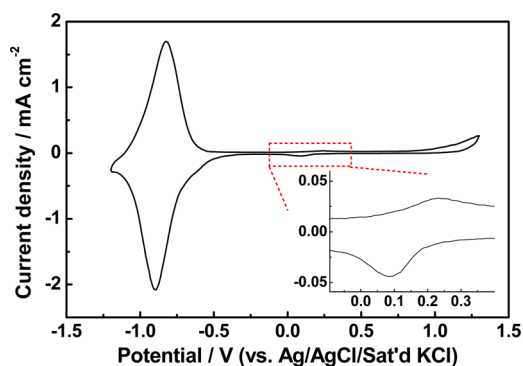


Figure 3. Cyclic voltammogram between 1.3 and -1.2 V of the polyCo film in 0.1 M $\text{KCl}_{(\text{aq})}$ at a scan rate of 100 mV s^{-1} . An obviously reversible redox couple at the formal potential ($E^{\circ'}$) of ca. -0.86 V is assigned to Co(II)/Co(I) . A small redox couple at $E^{\circ'}$ of ca. 0.16 V, referring to Co(II)/Co(III) , is observed as enlarged in the inset.

where n is the polymeric number of polyCo; Cl^- ions from the supporting electrolyte are responsible for charge neutralization of the films with Co ions as the redox centers. In addition, a weak Co(III)/Co(II) wave was observed as shown in the inset of Figure 3. The redox current of Co(III)/Co(II) was much smaller than that of Co(II)/Co(I) , which is attributed to the different self-electron-exchange ability. The self-exchange electron transfer rate constant of the former (2 $\text{M}^{-1} \text{S}^{-1}$) has been reported to be much smaller than that of the later (10^8 $\text{M}^{-1} \text{S}^{-1}$).³⁴ This has been occasionally observed for Co(tpy)_2 polymers.³⁵

In a supramolecular complex, electrons are localized in the metal d orbital with π symmetry. Since Co(I) is a richer electron donor than Co(II) , the increasing extent of splitting of the d orbital in the metal may result in stronger $d-d^*$ transitions that arise with a red shift from 520 to 560 nm. In the NIR region, highly intense absorption with a maximum located at around 1500 nm is observed. This absorption is attributed to the MLCT between the stronger electron donor of Co(I) and the good electron acceptor of the terpyridinyl group. As a consequence, the polyCo film in its reduced state exhibits broad absorption covering the UV–vis–NIR regions, which to the best of our knowledge is rare in electrochromic materials. In other words, a smart window using polyCo would be able to act as a shutter for both light and heat. While other materials, e.g., conjugated polymers, mostly shift their absorption among UV, visible, and NIR regions for electrochromism, they are not able to block heat sources from NIR light when in their darkened state for visible light. It should be noted that heat sources have contributions from both solar radiation (corresponding to a spectrum originating from 4500 K) and room radiation (~ 298 K). This material will be especially suitable to block the heat transmission from solar radiation according to the spectrum range.

Figure 4 shows the effect of the pH on the absorption of a polyCo film. For an as-deposited film immersed in a neutral or acidic solution, no obvious color change or spectral differences were found. However, when the film is immersed in an alkaline solution (pH 9–13), it quickly bleaches as shown in Figure 4b–e. The color change also depends on the film thickness. For $a \approx 800$ nm thick film, it takes on average less than 10 s for the film to change color once it is in contact with the solution. According to the spectra shown in Figure 4a, bleaching results

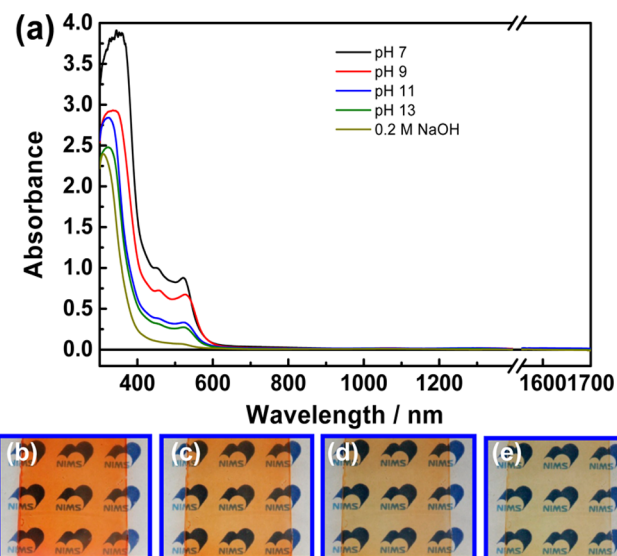
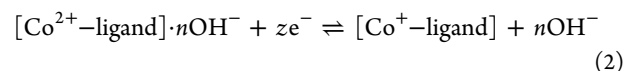


Figure 4. (a) UV–vis–NIR absorbance spectra of a polyCo film spray cast on ITO immersed in 0.1 M $\text{KCl}_{(\text{aq})}$ under different pH conditions. Corresponding photographs of the film in a solution with pH (b) 7, (c) 9, (d) 11, and (e) 13. Absorption data at wavelengths ranging from 1395 to 1555 nm have been removed for clarity because of the interference of water molecules.

from the weakened $d-d^*$ transition of Co(II) in the polyCo. Since the absorption peak of the polymer does not shift even when immersed in a 0.2 M NaOH solution, we link this phenomenon to the dipole of the hydroxide ions affecting the d orbital electrons and reducing the probability of the $d-d^*$ transition. Similar behavior was also observed for the solution phase of polyCo polymer (Figure S3). When the Co polymer was dissolved in water and the UV–vis spectra were measured with the addition of HCl or NaOH , there was no obvious change in the intensity of the peak of the $d-d^*$ transition when HCl was added, but there was a significant decrease in the intensity of the peak with the addition of NaOH . In fact, the partially filled d subshell of the Co ion leads to its high activity for ligand complexes or catalysis, and thus, it is sensitive to the presence of the hydroxide ions.

The electrochemical and physical stabilities of the polyCo film were also examined to confirm no decomposition of the film switched in alkaline solution. The films all maintained surfaces as smooth as the as-deposited film (Figure S4) switched in alkaline solution. The redox between Co(II) and Co(I) in the polyCo film was a reversible reaction within the investigated pH range as shown in Figure 5a. The pOH-dependent shifts in the half-wave potential ($E_{1/2}$) of the Co(II/I) redox reaction are summarized in Figure 5b (here we use pOH for better understanding). The $E_{1/2}$ of polyCo is constant at low hydroxide ion concentration (pOH > 8) and starts to change with a linear decrease in the pOH. Irregular change is found at pOH values lower than 4 due to high hydroxide ion concentration. Assuming that n molecules of hydroxide ion playing as a counterion involve in the redox reaction of polyCo as



The linear $E_{1/2}$ change with pOH can be described by the Nernst equation

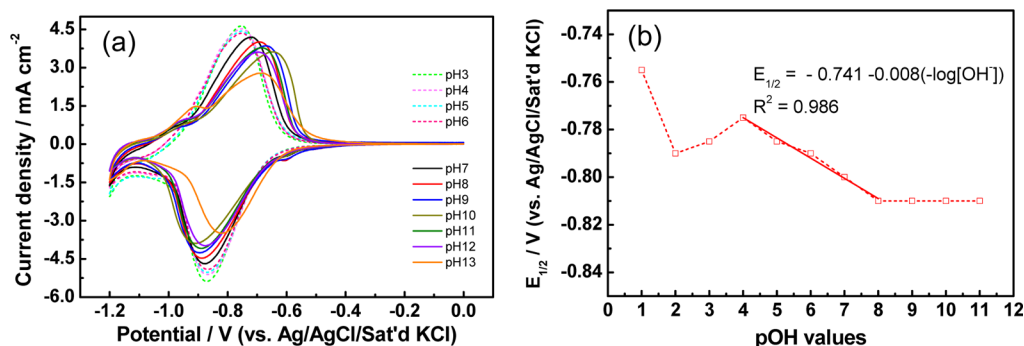


Figure 5. (a) Cyclic voltammogram between 0 and -1.2 V of the polyCo film in 0.1 M $\text{KCl}_{(\text{aq})}$ under different pH conditions adjusted by the addition of HCl or NaOH. (b) Corresponding $E_{1/2}$ as a function of pOH.

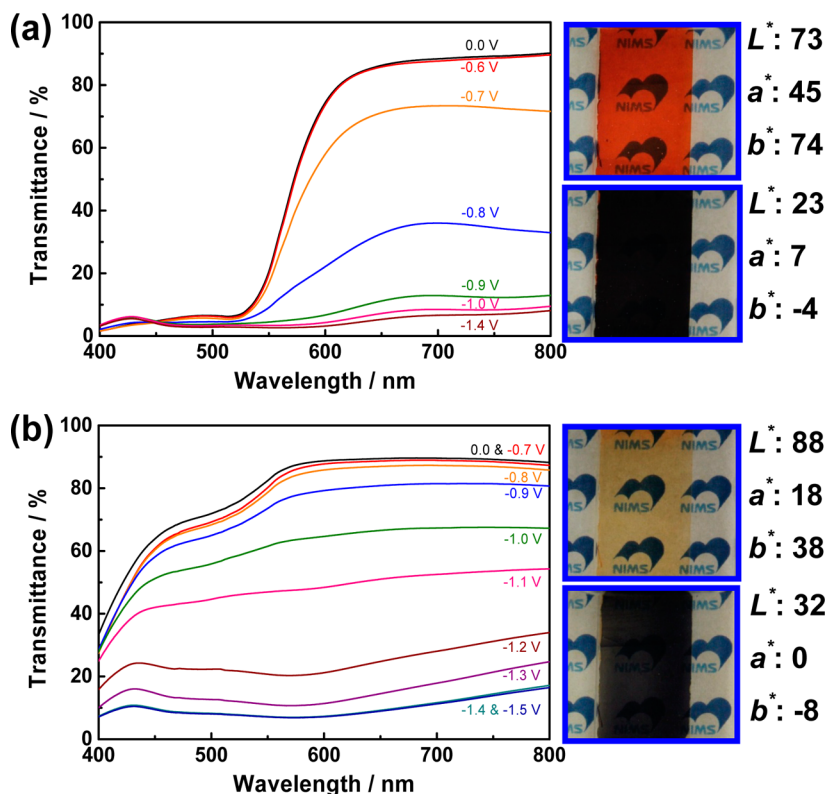


Figure 6. In situ transmittance spectral change at visible wavelengths of a polyCo film spray cast on ITO glass at various applied potentials in 0.1 M $\text{KCl}_{(\text{aq})}$ of pH (a) 7 and (b) 13. Corresponding photographs of the bleached and darkened polyCo films for each pH were taken for potentials of 0.0 and -1.3 V, respectively.

$$\begin{aligned}
 E &= E^0 - \frac{0.05916}{z} \log \frac{[\text{Co}^+ - \text{ligand}]}{[\text{Co}^+ - \text{ligand}][\text{OH}^-]^n} \\
 &= E^0 - \frac{0.05916}{zn} \log \frac{[\text{Co}^{2+} - \text{ligand}]}{[\text{Co}^+ - \text{ligand}][\text{OH}^-]} \quad (3)
 \end{aligned}$$

where z presents the electron transfer number affected by the hydroxide ions and $[\text{Co}^{2+} - \text{ligand}]$ symbolizes the repeating unit of polyCo. According to the slope fitted between pOH 4 to 8 (Figure 5b) and assuming z equals 1, the n value is calculated to be ca. 7.4. This result indicates that the detachment/attachment of ca. 7.4 molecules of hydroxide ions is included per one electron transfer between Co(II) and Co(I) in polyCo. This is evidence that hydroxyl ions are participating in the redox reactions of polyCo.

On the basis of this finding, we are interested in the electrochromic performance of polyCo films switched in alkaline solution. The transmittance spectra during the electrochromic reaction of the films in pH 7 and 13 solutions were recorded as shown in Figure 6. In a pH 7 solution, the spectrum of the bleached film (0.0 V) can be roughly described by dividing the spectrum into two parts at a wavelength of 600 nm. The film exhibits a high transmittance of 80 – 90% above 600 nm and a low transmittance of less than 10% below 600 nm. Such behavior is consistent with the absorption spectra shown in Figure 2 and lends the film an orange color as shown in the upper photograph in Figure 6a. The film is fully darkened at -1.4 V, and the transmittances in the visible light region (400 – 800 nm) are all lower than 10% (the highest is 7.8% at 800 nm), which makes the film take on a deep black color (lower photograph in Figure 6a). When the film is switched in a

pH 13 solution, the transmittance of the bleached film at wavelengths below 600 nm increases considerably, and the film is more transparent as shown in the upper photograph in Figure 6b. In the darkened state of the film, although the transmittances are slightly higher than those of the film in the pH 7 solution, the transmittances are still all lower than 20% in the visible light region (the highest is 16.5% at 800 nm). Consequently, the bleached polyCo film exhibits a more transparent color in the pH 13 solution ($L^* = 88$, $a^* = 18$, $b^* = 38$) than in the pH 7 solution ($L^* = 73$, $a^* = 45$, $b^* = 74$). In contrast, the darkened film has a stable black color in the pH 13 solution ($L^* = 32$, $a^* = 0$, $b^* = -8$) comparable with that in the pH 7 solution ($L^* = 23$, $a^* = 7$, $b^* = -4$). As shown in Figure 6b, the spray-cast polyCo film is light yellow and highly transparent to the human eye in its oxidized state; it attains a remarkably deep black color when reduced. The black-to-transmissive electrochromism can be achieved with switching in an alkaline aqueous solution.

Considering the usability of a black-to-transmissive display, the electrochromic responses at 500 nm were recorded as a reference because the human eye is most sensitive to this wavelength. As shown in Figure 7, the optical attenuation of

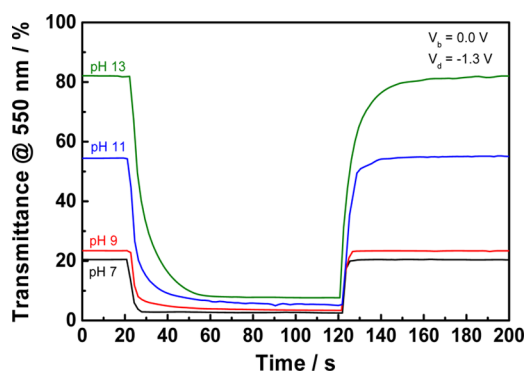


Figure 7. In situ transmittance responses at 550 nm of a polyCo film spray cast on ITO glass at applied potential steps of 0.0 and -1.3 V in 0.1 M $\text{KCl}_{(\text{aq})}$ of pH 7, 9, 11, and 13.

polyCo film is gradually enhanced in alkaline solutions mainly because of the improvement in the bleached transmittance (20.6% in pH 7 solution vs 81.9% in pH 13 solution). The electrochromic parameters are summarized in Table 1. A

Table 1. Electrochromic Performance of polyCo Film Switching in Different pH Solutions^a

pH	$T_{550,b}$ [%]	$T_{550,d}$ [%]	ΔT_{550} [%]	t_b [s]	t_d [s]
7	20.6	2.5	18.1	3.3	6.0
9	23.4	3.6	19.8	4.6	21.9
11	54.3	5.0	49.3	11.1	28.8
13	81.9	7.6	74.3	23.6	31.5

^a $T_{550,b}$ and $T_{550,d}$: bleached and darkened transmittance at 550 nm, respectively. ΔT_{550} : $T_{550,b} - T_{550,d}$; t_b and t_d : bleaching and darkening response time, respectively, upon reaching 95% transmittance change.

transmittance change of 74.3% (81.9–7.6%) was measured when switching in pH 13 electrolyte solution, which is indicative of the excellent electrochromic contrast achieved. Note that the response time is greatly affected by the pH conditions. The switching times for the bleaching and darkening process in a neutral solution were calculated to be

3.3 and 6.0 s, respectively, for a 3 cm^2 film. With increasing pH of the electrolyte solution, both the bleaching and the darkening responses become slower. In the pH 13 solution, bleaching and darkening took 23.6 and 31.5 s, respectively. Consistent with our previous discussion, the weakened d–d* transition affected by hydroxide ions is attributed to the reduced ability of an electron jumping from one d orbital to another. Applying a potential to polyCo means that the redox reaction is thus correlated to the concentration of hydroxide ions as discussed in relation to Figure 5. In the electrochromic reaction, the ratio of the response times of films in different pH solutions to the logarithm of the hydroxide concentration also shows a positive relationship (Figure S5). This suggests that the pH dependence of the electrochemical reaction of polyCo reflects the electrochromic response.

Figure 8 shows a 100-step stability test of the polyCo film switching in pH 13 solution. The transmittance is recorded at

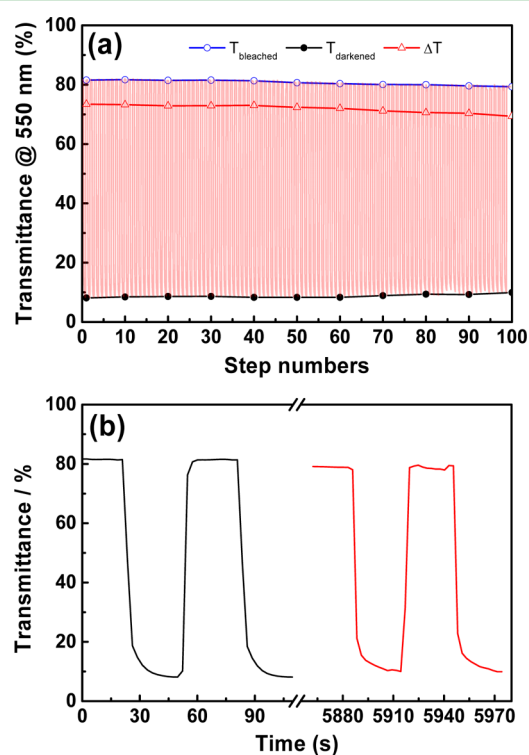


Figure 8. (a) Stability test via potential stepping between 0.0 and -1.3 V of a polyCo film spray cast on ITO glass in 0.1 M $\text{KCl}_{(\text{aq})}$ of pH 13 and with a switching time of 30 s. (b) Enlarged view of the first and final two steps.

550 nm, while the potential is stepped between 0.0 and -1.3 V for bleaching and darkening, respectively. Each step is set for 30 s to ensure completion of the electrochromic reaction. After 100 steps, the film exhibits stable color changes, and the switching response as shown in Figure 8b has not been prolonged. The transmittance change is about 73% (from 81% to 8%) in the first step; after 100 steps, it has decreased to $\sim 69\%$ (from 79% to 10%). However, the transmittance change of the film is still within 94.5% of its initial performance. This film can be considered to have good switching stability in an aqueous alkaline solution of pH 13. Since we obtained a highly stable switching in high pH, we can understand that the hydroxide ions ($\text{O}-\text{H}^-$) did not replace the N–Co bond in the polymer.

CONCLUSIONS

In summary, the metallo-supramolecular polymer film polyCo absorbs a wide range of light from the UV to the NIR (300–1700 nm) in its reduced state by applying a potential of -1.3 V (vs Ag/AgCl/satd KCl). By increasing the pH of the neutral aqueous electrolyte solution, the d–d* transition of the polymer is affected by the interaction between the d-orbital electron and hydroxide ions. The absorption of the film in alkaline solution is reduced for better transparency. As a consequence, the film exhibits wide-range attenuation of light by electrochemical redox switching. A black-to-transmissive electrochromism of the polyCo film switched in pH 13 aqueous electrolyte can thus be achieved with a transmittance change of 74.3% (81.9–7.6%) at 550 nm. A switching test between 0.0 and -1.3 V for 100 steps shows the film has good electrochromic stability, and the transmittance change remains within 94.5% of the initial value. However, the response times become longer in pH 13 solution ($t_b = 23.6$ s; $t_d = 31.5$ s) in comparison to those in a pH 7 solution ($t_b = 3.3$ s; $t_d = 6.0$ s) because of the weakened electron transfer ability associated with higher concentrations of hydroxide ions. Further efforts to improve the response time of this black-to-transmissive electrochromic material should be made. The black-to-transmissive electrochromic material is applicable to wide display devices including digital signage, e-paper, and smart windows in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02990.

SEM cross-sectional images of the as-prepared polyCo films, cyclic voltammogram between 0 and -1.2 V of the as-prepared polyCo film in 0.1 M KCl(aq) for the first 3 cycles, UV–vis absorbance spectra of 0.05 mg mL⁻¹ polyCo dissolved in water with addition of HCl or NaOH in different concentrations, SEM topographical images of the polyCo films with different conditions, ratios of the logarithm of hydroxide molar concentration, bleaching, and darkening response times in different pH solutions versus in pH 7 as standard (PDF)

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Notes

The authors declare no competing financial interest.

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