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SPECIAL SECTION PAPER

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Electrochromic devices using Fe(II)-based metallo-supramolecular polymer: Introduction of ionic liquid as electrolyte to enhance the thermal stability

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Abstract

We fabricated electrochromic (EC) devices with Fe(II)-based metallo-supramolecular polymer (polyFe), 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (BMPyr(NTf)$_2$) ionic liquid (**IL**), and Prussian blue (PB) as electrochromic layer, electrolyte layer, and counter layer, respectively. Thermal stability and ionic conductivity of BMPyr(NTf)$_2$ **IL** was measured by thermogravimetric analysis (TGA) and impedance analysis to be 380°C and approximately 7.8×10^{-4} S/cm, respectively. The fabricated device showed reversible electrochromism between bluish-violet and colorless by applying +3.0/−1.5 V alternately. The 65% of the original EC contrast remained in the device after the repeated changes for 100 cycles at 100°C.

KEYWORDS

device, electrochromism, ionic liquid, polyFe, thermal stability

1 | INTRODUCTION

Reversible color change phenomenon by the external electric stimulus is called electrochromism.[1–4] Electrochromic (EC) devices have received great attention owing to strong demands in various applications such as smart windows, digital signage, and antiglare rearview mirrors..[5–8] In addition to EC materials such as metal oxides, conjugated polymers, metal complexes, and arylamine-based polymers,[9] we found electrochromism of metallo-supramolecular polymers (MSPs).[7,10–14] Fe(II)-based MSP (polyFe) has reversible redox properties, large EC contrast, quick response, and high coloration efficiency.[10,11]

Our group reported EC devices with polyFe before. A mixture of polymethylmethacrylate (PMMA), propylene carbonate, $LiClO_4$, and acetonitrile was used as the electrolyte in the devices.[12–14] Thermal stability of EC device is required for the smart window application in the car, but the electrolyte does not have stability at high temperature.

An object of this paper is to investigate thermal stability of the EC device at 100°C by the introduction of ionic liquid (**IL**) as the electrolyte, because **IL**s have nonvolatility, nonflammability, high ionic conductivity, wide potential windows, and high chemical and thermal stability behavior.[15–17] We chose a combination of polyFe as the EC layer on working electrode, Prussian blue (PB) as the ion storage layer on counter electrode, and 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide (BMPyr(NTf)$_2$) **IL** as the electrolyte. We fabricated the EC devices and monitored reversibility for the repeated color changes at 100°C by UV-vis spectroscopy. We chose BMPyr(NTf)$_2$ among many **IL**s, because we found the polyFe layer and the PB layer are not soluble in $BMPyr(NTf)_2$ during the EC changes even at high temperature.

2 | EXPERIMENTAL SECTION

2.1 | Materials and instruments

Iron(II) acetate ($Fe(OAc)_2 > 99.99\%$) and PB ($Fe_4[FeCN_6]_3$) were purchased from Sigma-Aldrich; 1,4-di[[2,2′:6′,2″-terpyridin]-4′-yl]benzene, 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ($BMPyr(NTf)_2$) were supplied by Kanto Chemical Co, Inc. Methanol (MeOH) and acetic acid (AcOH) were supplied by Wako Chemical Corporation.

All electrochemical studies were carried out using an ALS/CHI electrochemical workstation (CH Instruments, Inc, USA) using two electrode system. An integrated Ocean Optics modular spectrometer was connected with the electrochemical analyzer to monitoring transmittance spectral change of the EC device upon application of the potential. Apeiros API Corporation automated spray coater was used for polyFe film preparation. AC spin coater machine was used for thin PB film preparation. Thermogravimetric analysis (TGA) was performed using an SII TG/DTA 6200 instrument in an N_2 environment with a 10°C/min heating rate. Impedance study was carried out by VersaSTAT4 electrochemical workstation (AMETEK, Princeton Applied Research, USA) using two electrode system. X-ray photoemission spectroscopy (XPS) study was conducted by ULVAC PHI, 5000 VersaProbe II X-ray source system using A1 Kα X-ray source ($h\nu = 1486.8$ eV) monochromator.

2.2 | PolyFe film preparation

Our previously reported procedure was followed to the synthesis of polyFe.[10,11] A solution of polyFe (3.5 mg/mL) was prepared by dissolving solid deep blue polyFe to methanol solvent. Prior to making polymer films, the ITO-glass substrates were cleaned by ultrasonication in acetone and then exposed to ultraviolet-ozone for 20 minutes. Finally, uniform deep blue colored polyFe films were prepared by using an automated spray coater machine on ITO-glass substrates with active area 1.0×0.8 cm^2.

2.3 | PB film preparation

To modify the counter electrode in EC device, a thin film of PB was prepared on ITO-glass substrates. Thin PB layers were prepared on 2.5×2.5 cm^2 ITO-glass substrates by the spin coating technique from a 10 mg/mL of water solution of PB.

2.4 | EC device fabrication

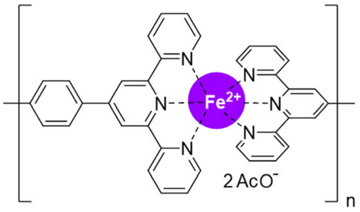
The thickness of polyFe film (390 ± 100 nm) and PB film (17 ± 3 nm) was determined by surface profiler analysis (Figure S1). To fabricate an EC device, 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ($BMPyr(NTf)_2$) **IL** placed in between polyFe and PB-coated ITO-glass in sandwich configuration manner. Finally, the device was sealed with silicon glue to protect from atmospheric conditions. Different potentials were applied to positive and negative electrode to observe color changes between bluish-violet and colorless.

3 | RESULT AND DISCUSSION

The chemical structure of polyFe is shown in Scheme 1, where Fe(II) ions are coordinately bounded by bis-terpyridine ligand to form quasi-octahedral geometry, acetate ion ($^-$OAc) make corresponding charge balance of the polymer. PolyFe shows strong blueish-violet color with an absorption band in the visible region around 590 nm. The bright blue color is attributed to the metal-to-ligand charge transfer (MLCT) transition of the central Fe^{2+}-metal ion in the quasi-octahedral coordination geometry constituted by the bis-terpyridine ligands.[10,11]

The elemental composition of the polyFe film surface was characterized by XPS analysis in Figure S2. The peaks at 285, 400, 532, and 709 to 722 eV in the wide scan of XPS study prove the presence of C, N, O, and Fe, respectively. The area under peaks provided the N to Fe atomic ratio in polymer chain approximately 5.9:1 (N:Fe).

The thermal stability of $BMPyr(NTf)_2$ **IL** was evaluated by TGA study in the N_2-saturated atmosphere in Figure S3. TGA study of **IL** shows thermal stability up to approximately 380°C. The ionic conductivity of **IL** was measured by impedance study at room temperature in Figure S4. The calculated ionic conductivity from the Nyquist plot showing approximately 7.8×10^{-4} S/cm.



SCHEME 1 The chemical structure of polyFe

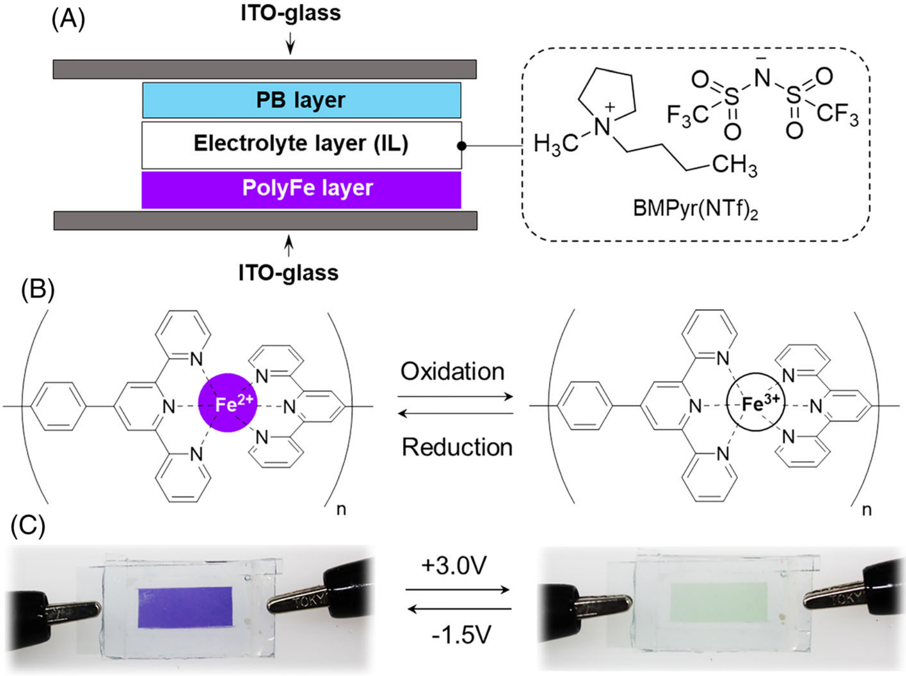


FIGURE 1 A, Schematic presentation of the fabricated electrochromic (EC) device. B, Change of chemical structure of polyFe upon oxidation and reduction. C, Color change in device redox by applying voltage +3.0/−1.5 V

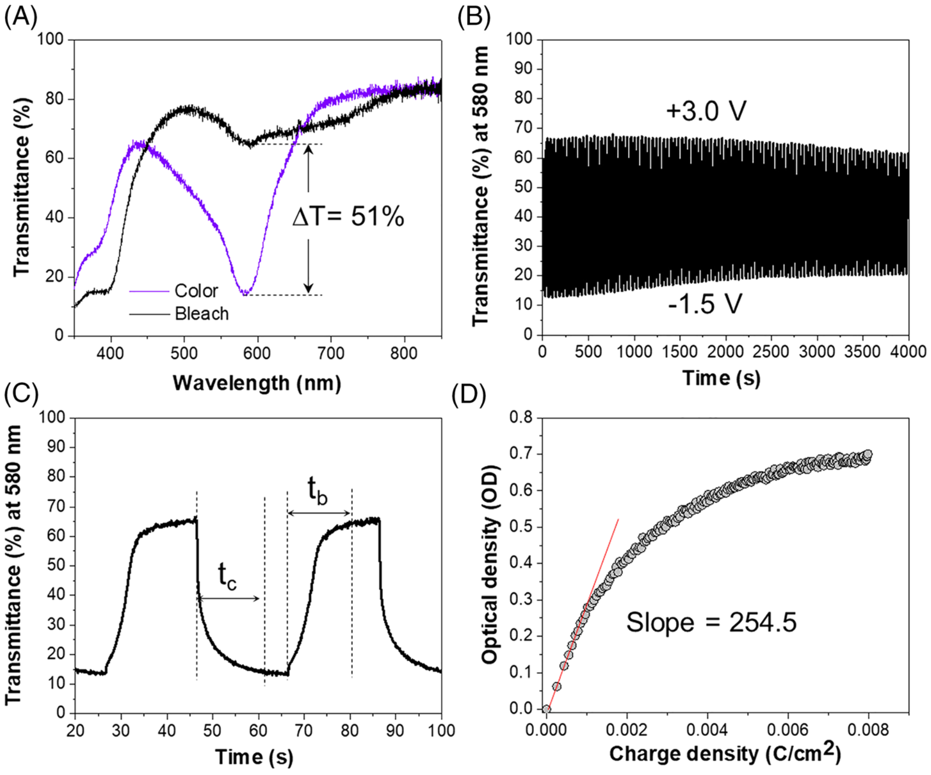


FIGURE 2 A, Change of transmittance ($\Delta T\%$); B, transmittance versus time ($T - t$) behavior; C, enlarge $T - t$ spectra; D, plot of optical density versus charge density of fabricated device

3.1 | EC device and electrochromism

The schematic description of the fabricated EC device was represented in Figure 1A, where a spray-coated polyFe film serves as an EC layer on working electrode side, spin-coated thin PB layer work as ion storage layer on counter electrode side, and drop-casted BMPyr(NTf)$_2$ **IL** worked as an electrolyte to connect these two electrodes electrochemically. Upon applying positive bias (+3.0 V) on fabricated EC device, the metal center of polyFe was oxidized from Fe^{2+} to Fe^{3+} lead the color change from blueish-violet to colorless. Again, upon applying negative bias (−1.5 V), Fe^{3+} turns back to Fe^{2+}, which caused a color change from transparent to blueish-violet.

The change of chemical structure and color change of device are shown in Figure 1B,C, respectively. In order to investigate the EC nature of **IL**-based EC device, spectroelectrochemical analyses were carried out at room temperature in Figure 2. The spectral transmittance changes of EC device upon application of potential are shown in Figure 2A. BMPyr(NTf)$_2$ **IL**–based fabricated device shows bleaching and coloration by the application of +3.0 V and −1.5 V, respectively. The change of transmittance (ΔT%) between the bleached and colored state was calculated approximately 51%, monitoring at 580 nm (the MLCT peak maxima for polyFe). The dynamic transmittance switching ($T - t$ behavior) was recorded by monitoring at 580 nm upon the fixed operation voltage of +3.0/−1.5 V with 20-second intervals (Figure 2B). The fabricated device showed a slow response with bleaching time of 20.5 seconds and coloration time of 12 seconds (for 95% change in ΔT) in Figure 2C.

The corresponding current flow with time ($I - t$) during electrochromism by applying the voltage is exposed in Figure S5. Initially, device showing higher current value, after a certain time, the current value decreases and attends a steady performance at room temperature. The coloration efficiency (η) of BMPyr(NTf)$_2$ **IL**–based device was calculated approximately 254.5 cm^2/C by considering the change of optical density with charge density in Figure 2D using Equation (1):

$$\eta = \frac{\Delta OD}{Q_d} = \frac{\log\left(\frac{T_b}{T_c}\right)}{Q_d}, \tag{1}$$

where η = coloration efficiency (cm^2/C), ΔOD = change of optical density, T_b and T_c are the transmittance value at the bleached state and colored state, respectively, at wavelength 580 nm, and Q_d = charge density (C/cm^2).

We reported coloration efficiency of a polyFe film in acetonitrile solution of LiClO$_4$ was 263.8 cm^2/C in our previous paper.[18]

3.2 | Thermal stability of IL-based EC device

We have measured the EC performance of the BMPyr(NTf)$_2$ **IL**–based device at room temperature, followed by at 100°C, 40%RH, then again at room temperature (Figure 3). We have compared the EC performance of the device before and after the repeated operation at 100°C. In Figure 3A, initial 100 *T-t* cycles were recorded at 25°C, followed by 80 cycles at 100°C and again 100 cycles at 25°C from the same device by applying +3.0 and −1.5 V of operating voltage with 20-second intervals. By considering transmittance change before and after 100°C temperature and using the following equation (2), we have evaluated approximately 65% of device stability in terms of EC properties retention.

$$\%of\ EC\ properties\ retention = \frac{\Delta T_{after}}{\Delta T_{before}} \times 100. \tag{2}$$

Transmittance change (ΔT) and response time (t_b, t_c) of the device before and after 100°C operations were

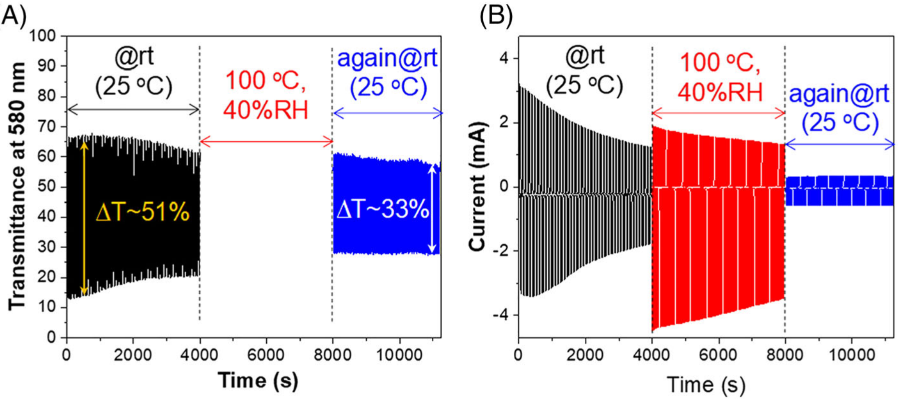


FIGURE 3 A, Transmittance change with time ($T - t$); B, corresponding current flow with time ($I - t$) through device upon applying operating voltage +3.0 and −1.5 V repeatedly at room temperature, 100°C, 40% RH, again room temperature

TABLE 1 Summary of EC properties of device before, during, and after 100°C treatment

Properties	Change of Transmittance, ΔT	Current Response, mA		Response Time, s	
		+ve	−ve	t_c	t_b
Before 100°C	~51.0%	3.1 to 1.2	−3.4 to −1.7	12.3	20.52
During 100°C	---	1.9 to 1.3	−4.4 to −3.4	---	---
After 100°C	~32.5%	0.32 to 0.3	−0.56 to −0.56	13	21.2

summarized in Table 1. The corresponding current follows of EC device at 25°C, 100°C and followed by again at 25°C were recorded in Figure 3B. In $I-t$ behavior, current response has decreased after a certain time and attends a steady performance at room temperature. In our previous EC device using PMMA, propylene carbonate, $LiClO_4$, and acetonitrile-based gel as an electrolyte, we could not observe any color change after the treatment at 100°C, probably due to gel dryness and bubble formation. However, in this work, the device shows color change after the EC treatment at 100°C.

4 | CONCLUSIONS

We have successfully fabricated EC devices based with $BMPyr(NTf)_2$ **IL** as a viscous electrolyte layer, cathodically coloring polyFe as the EC layer on the working electrode side and PB as ion storage layer on the counter electrode side. PolyFe film shows bright bluish-violet color with absorbance maxima at approximately 580 nm. The chemical composition (5.9:1, N to Fe atomic ratio) of polyFe has been confirmed by the XPS study. Importantly, the thermal stability of $BMPyr(NTf)_2$ **IL** shows up to 380°C temperature without any weight loss and ionic conductivity of approximately 7.8×10^{-4} S/cm. Fabricated EC device revealed the reversible color change from bluish-violet to colorless with approximately 51% transmittance change by applying voltage 3.0/−1.5 V repeatedly in a little slow response. Fabricated device shows a coloration efficiency of 254.5 cm^2/C at room temperature. Thermal stability of $BMPyr(NTf)_2$ **IL**–based EC devices has been evaluated at 100°C temperature with 65% property retention. This study could help for high-temperature–operated EC devices fabrication in the future.

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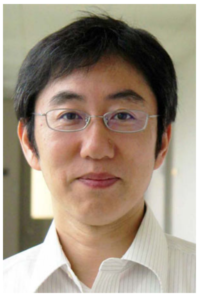

Dr Masayoshi Higuchi graduated from the Department of Applied Fine Chemistry, Osaka University, in 1993 and was awarded Master of Engineering in 1995 and Doctor of Engineering in 1998 at the same university. He was appointed Research Associate at Department of Chemistry, Keio University in 1998 and promoted to Assistant Professor in 2003. He then moved to National Institute for Materials Science (NIMS), Japan, in 2004. He has been Group Leader since 2009. His current research is focused on synthesis, properties, and device fabrication of metallo-supramolecular polymers.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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