Electrochemical Control of Emission and Coloration with High Response and Durability by Introduction of Counter Reaction Material

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An electroswitching device that enables modulation of both photoluminescence and coloration was obtained. The device consisted of luminescent lanthanide(III) complex Eu(hfa)₃(TPPO)₂ (photoluminescence material) and a diheptyl viologen HV²⁺ (electrochromic material). Coloration and emission control were achieved by only electrochemical reactions of HV²⁺. The coloration of the device was controlled by HV²⁺ electrochromism. Photoluminescence control was also achieved by the HV²⁺ electrochromism via intermolecular energy transfer from the excited states of Eu(III) ions to colored HV⁺⁺. However, there were some problems that the response time of switching between emission and coloration was quite slow (approximately 15 minutes), and the representation stability of switching between emission and coloration was low. These problems would be caused by absence of counter electrode reaction material against HV²⁺ redox. In order to improve the response time of the cell and decrease the driving voltage for dual-mode representation, we introduced prussian blue (PB) modified electrode as an electrochromical counter redox material.

Keywords: Electrochemical modulation, Electrochromism, Eu(III) complex, High response, High durability

1. Introduction

Materials with multifunctional response to external stimuli such as photo, thermal, and electric stimuli have recently attracted much attention because they can be used to develop chemical and biochemical sensors [1,2], molecular logic gates [3], and display devices [4]. Materials displaying both fluorescence and absorption switching have been reported.

Among the various possible stimuli that may be used for multifunctional materials, we focused on electrical stimuli because they can be applied rapidly, remotely, and reversibly while maintaining mild conditions suitable for biological systems [5]. Electrochromic (EC) materials that change reversibly their color as a result of electrochemical redox reactions are potential candidates for multifunctional devices because they have been successfully applied to optoelectronic devices [6], smart windows [7], dimming mirrors [8], EC tags, and digital signage, and also have the advantage of low power consumption. We have shown that both emission and absorption can be controlled through electrochemical reactions by fabricating multifunctional systems in which a luminescent Eu(III) complex and an electrochemically active material, viologen derivatives, have been integrated (Fig. 1 and Fig. 2) [9-16]. Generally, Eu(III) complexes have unique optical properties (line-like red emissions, long luminescence lifetimes, high transparency in the visible region (large Stokes shift), and high luminescence quantum yields), which have resulted in their widespread application in phosphors, bioassays, and sensor development.
In the system developed by us, fluorescence switching was caused by FRET between the luminescent Eu(III) complex and viologen derivatives in response to electrical stimuli of viologen derivatives [15,16]. However, upon the application of long-term electrical stimuli, most of these systems, including our previous system, lack a quick response, high reversibility, and high contrast of the fluorescence. Since electrochemical switching of fluorescence and absorption in combining Eu(III) complex and HV\(^2^+\) (denoted as Eu(III)complex/HV\(^2^+\), see Fig. 1 for chemical structures) solution is time-consuming (over 100 s), it is important to improve electroswitching performance.

In this paper, we report the electrochemical control of coloration and emission, with a quick response and high reversibility, for a novel electrochemical cell. Problems pertaining to responsivity and reversibility in the case of our previous system were caused by the absence of counter electrode materials that could accelerate redox reactions of EC materials. The cell reported here contains a luminescent Eu(III) complex (tris(hexafluoroacetylacetonato) europium-bis(triphenylphosphine oxide): Eu(hfa)\(_3\)(TPPO)\(_2\)) and the EC materials HV\(^2^+\) and Prussian blue (PB). PB is cyan in the oxidized state and colorless in the reduced state [19]. Thus, when HV\(^2^+\) turns cyan upon reduction, the PB-modified counter electrode also turns cyan upon oxidation, thereby improving the color contrast between the colored and transparent states of the cell. Thus, control of both coloration and emission is achieved solely through electrochromism of HV\(^2^+\) and PB. Control of photoluminescence was also achieved as a result of HV\(^2^+\) and/or PB electrochromism via FRET from the excited states of Eu(III) ions to colored HV\(^+\) and/or PB. In addition, the PB modified electrode must act as a counter electrode for the HV\(^2^+\) redox reaction to facilitate a quick response and high switching stability of the cell. Therefore, the response time and reversibility are expected to be improved by the effect of a redox reaction involving HV\(^2^+\).

Fig. 1. Chemical structures of luminescent Eu\(^{3+}\) complex and HV\(^{2+}\).

### 2. Experimental

#### 2.1. Materials

Europium acetate tetrahydrate, hexafluoroacetylacetonate (hfa), and triphenylphosphine oxide (TPPO) were purchased from Tokyo Kasei Industries Ltd. 1,1'-diheptyl-4,4'-bipyridinium dibromide (HV\(^2^+\)) was purchased from Aldrich Co. Ltd. and used as a EC material. Iron(III) chloride hexahydrate (FeCl\(_3\)∙6H\(_2\)O) (Wako Pure Chemical Industries Ltd.) and potassium ferricyanide (K\(_3\)Fe(CN)\(_6\)) (Wako Pure Chemical Industries Ltd.) were used for preparation of PB modified electrode. Propylene carbonate (PC) (Kanto Chemical Co., Inc.) and sulfuric acid (H\(_2\)SO\(_4\)) (Kanto Chemical Co. Inc.) were used as received. Lithium perchlorate (LiClO\(_4\)) (Wako Pure Chemical Industries Ltd.) was used as supporting electrolyte without purification. Indium tin oxide (ITO) (Yasuda, 10 Ω/sq) was also obtained and prepared by washing with detergent in an ultrasonic bath, followed by cleaning in deionized water twice and then acetone (each sequence lasting 20 min).

#### 2.2. Synthesis

**2.2.1. Tris(hexafluoroacetylacetonato)europium \([\text{Eu(hfa)}_3\text{(H}_2\text{O)}_2]\) complex**

Europium acetate n-hydrate (6.0 g, 15.0 mmol) was dissolved in 60 mL of deionized water in a conical flask while stirring at room temperature, followed by the dropwise addition of liquid hfac-H\(_2\) (8.4 g, 40.3 mmol). The white powder obtained after stirring for 3 h was filtered and recrystallized from methanol/water to give the title compound in 85% yield. IR (KBr, cm\(^{-1}\)): 1649 (st, C=O stretch), 1254–1140 (st, C–F). Anal. calcd. for C\(_{15}\)H\(_7\)O\(_8\)F\(_{18}\)Eu: C, 22.48; H, 0.88%. Found: C, 22.12; H 1.05%.
2.2.2. Tris(hexafluoroacetylacetonato)europium(III) bis(triphenylphospine oxide) \([\text{Eu(hfa)}_3(\text{TPPO})_2]\) complex

\(\text{Eu(hfa)}_3(\text{TPPO})_2\) was synthesized per a previously reported method [9]. A solution of \(\text{Eu(hfa)}_3(\text{H}_2\text{O})_2\) (4.28 g, 6 mmol) and TPPO (2.78 g, 10 mmol) in methanol (100 mL) was refluxed for 12 h, followed by concentration using evaporator. The resulting yellow needle-like crystals were recrystallized from methanol. IR (KBr, cm\(^{-1}\)): 1653 (st, C=O stretch), 1254–1140 (st, C–F), 1121 (st, P=O). Anal. calcd. for \(\text{C}_{51}\text{H}_{33}\text{O}_8\text{F}_{18}\text{P}_2\text{Eu}\): C, 45.96; H, 2.50%. Found: C, 46.20; H, 2.38%.

2.3. Preparation of PB-modified electrode

Thoroughly washed ITO glass electrodes were further cleaned with UV-O\(_3\) for 20 min to ensure the complete removal of all organic substances. Electrochemical deposition of prussian blue (Fe\(_8\)\(^{III}\)[Fe\(_6\)\(^{II}\)(CN)\(_6\)])\(_3\), PB) modified electrode was performed on ITO glass electrode by galvanostatic electrodeposition process into the cell. The solution for electrodeposition was containing FeCl\(_3\)∙6H\(_2\)O (20 mmol/L) and K\(_3\)Fe(CN)\(_6\) (20 mmol/L) in 20 mmol/L H\(_2\)SO\(_4\) aqueous solution. During galvanostatic electrodeposition, ITO glass electrode was cathodically polarized (0.25 mA/cm\(^2\) for 30 s) in the solution, and a platinum wire was used as counter and reference electrode. After film deposition, the electrodes were washed with distilled water and dried under vacuum.

2.4. Construction of ITO/ITO and ITO/PB cell

The cell was constructed with ITO glass electrode and PB modified electrode (ITO/PB cell). The PC solution containing \(\text{Eu(hfa)}_3(\text{TPPO})_2\) (10 mmol/L), HV\(_2^+\) (10 mmol/L), and LiClO\(_4\) (200 mmol/L) was sandwiched between ITO electrode and PB modified electrode to evaluate the EC and photoluminescence properties. Inter electrode gap was kept with 70 \(\mu\)m by using plastic spacer (Lintec Co.). As the reference, the ITO/ITO cell with two ITO glasses electrodes was also fabricated.

2.5. Electrochemical measurements

Cyclic voltammograms and chronoamperometric measurement were recorded on a potentiostat/galvanostat (ALS, 660A) equipped with a computer. A three-electrode cell was constructed with an ITO glass electrode or PB modified electrode as working electrode, Pt wire as counter electrode and an Ag/AgCl electrode as reference. The scan rate was 50 mV/s. Absorption spectra were recorded in situ during the potential sweep using a diode array detection system (Ocean Optics, USB2000). Two electrode cells were constructed with an ITO glass as working electrode, and ITO glass electrode (ITO/ITO cell) or PB modified electrode (ITO/PB cell) as counter and reference. Response time tests of switching between coloring and bleaching were performed by applying -2.0 V (100 s) / 0 V (1,000 s) for ITO/ITO cell, -0.8 V (10 s) / 0 V (10 s) for ITO/PB cell. The solution for electrochemical studies was purged with nitrogen gas for 20 min before each experiment.

2.6. Photophysical measurements

Ultraviolet-visible (UV-vis) absorption spectra of the cells were measured using a spectrophotometer (JASCO, V-570). Path length of the cell was 70 \(\mu\)m. Photoluminescence spectra were obtained using a spectrofluorimeter (JASCO, FP-6600). Excitation wavelength of the cells was 337 nm. Switching stability tests of absorption (600 nm) and emission (615 nm) were performed by applying -0.8 V (10 s) / 1.4 V (10 s) for ITO/PB cell. The solution for optical measurements was purged with nitrogen gas for 20 min before each measurement.

3. Results and discussion

3.1. Electrochemical properties in three-electrode cell

In order to investigate the EC properties of the composite material, cyclic voltammograms (CVs) and changes in absorbance at 400, 600, and 700 nm were measured using ITO electrode. In Fig. 3(a), the \(\text{Eu(hfa)}_3(\text{TPPO})_2\) solution did not show obvious reduction and oxidation in the measured potential range of 1.0–0.8 V vs Ag/AgCl). For the HV\(_2^+\) solution (Fig. 3(b)), one reductive peak and a corresponding oxidative peak were observed at potentials of -0.7 and -0.31 V, respectively. As the reductive current increased from about -0.3 V, the absorbance of the HV\(_2^+\) solution at 400, 600, and 700 nm changed in a manner identical to that of the HV\(_2^+\) solution. In the absorption spectrum of the colored \(\text{Eu(hfa)}_3(\text{TPPO})_2/\text{HV}_2^+\) solution (Fig. 4(b)), new absorption bands observed at around 400 and 600
nm were in good agreement with those of the reduced HV$^{2+}$ (HV$^{3+}$) (Fig. 4(a)). The coloration of HV$^{2+}$ in the presence of the Eu(III) complex shows good agreement with the typical EC behavior of HV$^{2+}$ (Fig. 4(b)); thus, Eu(hfa)$_3$(TPPO)$_2$ does not significantly affect the EC behavior of HV$^{2+}$.

Further, the electrochemical reactivity of the PB-modified electrode was also analyzed in LiClO$_4$/PC solution containing HV$^{2+}$ and/or the Eu(III) complex (Fig. 5). During a potential sweep from the negative to positive direction in LiClO$_4$/PC solution, the CV curve of the solution showed an oxidative current from -0.2 V; the current reached a peak at +0.4 V, and absorbance at 400, 600, and 700 nm was higher than that at 0 V (Fig. 5(a)). In the absorption spectrum, a broad absorption band over 500 nm was observed (Fig. 6(a)). These changes in absorbance are a result of the oxidation of PB [19]. Compared to onset oxidation potential and the corresponding to the changes in absorbance at 400, 600, and 700 nm of the PB-modified working electrode in LiClO$_4$ solution (Fig. 5(a)), their values of the PB-modified working electrode in Eu(hfa)$_3$(TPPO)$_2$ (Fig. 5(b)), HV$^{2+}$ (Fig. 5(c)), and Eu(hfa)$_3$(TPPO)$_2$/HV$^{2+}$ solutions (Fig. 5(d)) were similar. In addition to this, absorption spectra of colored and bleached states of the PB-modified electrode in the Eu(hfa)$_3$(TPPO)$_2$
Fig. 5. Changes in absorbance at 400, 600, 700 nm (top) and cyclic voltammograms (bottom) of (a) Eu(hfa)₃(TPPO)₂, (b) HV²⁺, and (c) Eu(hfa)₃(TPPO)₂/HV²⁺ in a 0.2 mol/L LiClO₄/PC electrolyte using a PB-modified working electrode.

Fig. 6. Absorption spectra of bleached and colored state (0.4 V/10 s) using a PB-modified working electrode in (a) LiClO₄/PC solution and (b) Eu(hfa)₃(TPPO)₂/HV²⁺ in LiClO₄/PC solution (Coloring process was applied -0.65 V for 10 s).

solution (Fig. 6(b)) were almost similar to the PB-modified electrode in the LiClO₄ solution (Fig. 6(a)). Namely, the electrochemical reaction of HV²⁺ was not observed on the PB-modified electrode. These results suggest that the electrochemical reactivity of the PB-modified electrode was not affected by HV²⁺ or the Eu(III) complex, and that the conventional EC reaction of PB (eq.1) occurred [19].

\[
\text{MFe}^{III}[\text{Fe}^{II}(\text{CN})₆] + \text{M}^+ + e^- \rightleftharpoons \text{M₂Fe}^{II}[\text{Fe}^{II}(\text{CN})₆] \quad (\text{cyan color})
\]

\[
\text{(colorless)}
\]

(M: Li, Na, or K in PC)

3.2. Electrochemical properties in two-electrode cell

In order to investigate the electrochemical properties of the two-electrode cells (Fig. 7(a)), we measured the absorption change at 600 nm and CVs of the ITO/ITO and ITO/PB cells (Fig. 7(b)). For the former cell, the absorbance at 600 nm increased from -1.75 V as the current increased because of the electrochemical reduction of HV²⁺. On the other
hand, current flow in and coloration of the ITO/PB cell were observed from -0.35 V, indicating a dramatic decrease in the operation voltage when the PB modified electrode was used. This decrease in the operation voltage is likely caused by the use of a PB-modified electrode for the HV$^{2+}$ redox reaction. In the ITO/ITO cell, because a suitable counter electrode material for the HV$^{2+}$ redox reaction was not available, irreversible oxidation of the supporting electrolyte and solvent, or an undesirable side reaction, would have occurred at the counter electrode upon the reduction of HV$^{2+}$. In the ITO/PB cell, oxidation of PB can accompany the reduction of HV$^{2+}$, leading to the acceleration of HV$^{2+}$ reduction in the cell. The lower oxidation potential of PB (about 0 V, Fig. 5(a)) would be conducive to the coloration of the ITO/PB cell at a lower operation voltage compared to that of the ITO/ITO cell.

![Fig. 7](image)

Fig. 7. (a) ITO/ITO (left) and ITO/PB (right) two-electrode cells. (b) Change in absorbance (top) at 600 nm and cyclic voltammograms (bottom) of ITO/ITO cell (black dashed line) and the ITO/PB cell (blue line) containing HV$^{2+}$ and Eu(hfa)$_3$(TPPO)$_2$ in LiClO$_4$/PC solution.

Figure 8 shows the absorption spectra of the ITO/PB cell. When the bias voltage of 1.4 V was applied for 10 s, no absorption bands were observed in the visible region (400–700 nm), indicating that the cell was colorless (photo in Fig. 8). In contrast, when the bias voltage of -0.8 V was applied for 10 s, the cell color changed to cyan with the appearance of the new absorption bands at around 400, 600, and 700 nm. These absorption bands were assigned to both the reduced species (HV$^{+}$) and oxidized state of PB, suggesting that the color contrast of the cell would be improved by the co-coloration of HV$^{+}$ and PB (Fig. 9).

![Fig. 8](image)

Fig. 8. Absorption spectra of the ITO/PB cell (under bias voltage of 1.4 V (10 s) and -0.8 V (10 s) for the black dashed and blue lines, respectively) containing HV$^{2+}$ and Eu(hfa)$_3$(TPPO)$_2$ in LiClO$_4$/PC solution.

In order to investigate the response time of the coloring and bleaching processes of the ITO/ITO and ITO/PB cells, the absorption changes at 600 nm during the processes were measured (Fig. 10). In the case of the former cell without appropriate redox material at the counter electrode, the coloration process in the transparent state required the application of -2.0 V for 100 s to reach an absorbance of 0.4. The bleaching process required a longer time, 1000 s, even under short circuit (Fig. 9).
In contrast, coloration of the ITO/PB cell was achieved by application of -0.8 V for 10 s, and bleaching was complete within 10 s under short circuit (Fig. 10(b)). The response times of both coloration and bleaching of the ITO/PB cell were dramatically improved by the introduction of the PB-modified electrode, which acts as a counter reaction material [14]. The stable redox properties of the PB-modified electrode were responsible for the quantitatively balanced HV$^{2+}$ redox reaction. Consequently, the coloration and bleaching rates of the ITO/PB cell improved because the balanced redox system accelerated the electrochemical reaction of the cell.

![Fig. 10. Chromoabsorptometric curves of the (a) ITO/ITO and (b) ITO/PB two-electrode cells containing HV$^{2+}$ and Eu(hfa)$_3$(TPPO)$_2$ in LiClO$_4$/PC solution during the coloring (-2.0 V in ITO/ITO cell and -0.8 V in ITO/PB cell) and bleaching processes (open-circuit condition).](image)

In order to verify this effect by employing the PB film, the electrode potential of the working and counter electrodes is needed to be investigated when bias voltage is applied to the ITO/ITO and ITO/PB cell because the voltage is the difference of potential between a working and a counter electrode and does not show electrochemical circumstances of each electrode property. In this study, we used ALS model 660A potentiostat/galvanostat as voltage source and 440A potentiostat/galvanostat potentiometer as an electrometer for monitoring the electrode potential, respectively. The author connected up the working electrode terminal of 660A to the ITO working electrode, and the counter and reference electrode terminals to the ITO or PB-modified counter electrode for applying the voltage. This cell can be considered as the two-electrode cell with long inter-electrode distance of 10 mm. We connected up the working electrode terminal of 440A to the ITO electrode, the counter electrode terminal to the ITO or PB-modified counter electrode, and the reference electrode terminal to the Ag/AgCl reference electrode for measuring the working electrode potential of the ITO electrode (Fig. 11) [21]. We can obtain the electrode potentials of the ITO working electrode by measuring the electrode potentials while applying some voltage to the two-electrode cell. On the other hand, the potentials of ITO or PB-modified counter electrode were estimated from both the voltage and the potential of the working electrode. Further, the absorption change, CVs and electrode potential change of the working and counter electrode can be obtained.

![Fig. 11. System for electrode potential measurement in a two-electrode cell.](image)

Figure 12 showed the changes in the absorbance at 400, 600, 700 nm (top) and electrode potential vs.Ag/AgCl (middle), and current response of the two-electrode cell (bottom) of (a) ITO/ITO cell and (b) ITO/PB cell. As with the case of two electrode cell (path length was 75 μm), the absorbance at 400, 600, and 700 nm increased from -1.75 V as the current increased in the ITO/ITO two-electrode cell (path length was 10 mm) (Fig. 12(a)). From the
result of electrode potential change as shown in middle of Fig. 12(a), when the voltage of above -1.75 V is applied to cell, the electrode potential of working ITO maintained at about -0.5 V, while the electrode potential of counter ITO electrode increased. Comparing the result of two-electrode cell (path length was 10 mm) to the change in absorbance and CV of the three-electrode cell using ITO working electrode (Fig. 3), the increase of absorbance is due to the reduction of HV$_2^+$ on an ITO working electrode. In addition to this, when the bias voltage was over -1.75 V, the electrode potential of counter electrode was corresponded to the potential of solvent degradation, indicating that repetition stability of ITO/ITO two-electrode cell is low. On the other hand, the absorbance of ITO/PB two-electrode cell whose path length was 10 mm increase from -0.5 V (Fig. 12(b)). The behavior of changes in absorbance was also consistent with ITO/PB two-electrode cell whose path length was 75 μm as shown in Fig. 7(b). From the result of electrode potential change as shown in middle of Fig. 11(b), when the bias voltage was -0.5 V, the potential of ITO working electrode maintained at about -0.5 V, while the potential of PB-modified counter electrode was about 0 V. Given the result of changes in absorbance and CV of the three-electrode cell with ITO or PB-modified electrode as working electrode (Fig. 3 and Fig. 5), the increase of absorbance is likely to reduction of HV$_2^+$ on ITO electrode and oxidation of PB.

From studies on the electrode potential measurements, the dramatic decrease of coloration voltage was found to the oxidation of PB-modified counter electrode at low potential. As the consequence of low voltage for coloration and failure of solvent degradation, the response time and repetition stability of both emission and coloration would be improved than that of ITO/ITO electrode cell.

3.3. Photoluminescence control in two-electrode cell

Red emission of the Eu(III) complex in ITO/PB cell were observed at around 580, 590, 615, 650, and 700 nm under the excitation of the hfa ligands (337 nm) when the cell was clear colorless by applying the bias voltages of 1.4 V (Fig. 13). The emission of the cell was monitored from the ITO electrode side. These emission bands were attributed to the f-f transition $^5D_0 \rightarrow ^5F_J$ ($J = 0, 1, 2, 3, and 4$); this was considered as the “emission-on” state (photo in Fig. 13). When the cell was in the colored state (-0.8 V), the red emission of the Eu(III) complex was completely quenched, resulting in an “emission-off” state (photo in Fig. 13). In the case of the ITO/PB cell without HV$_2^+$, the emission intensity of the Eu(III) complex was not influenced by the application of a voltage (Fig. 14). Therefore, the quenching of the emission was caused by the colored HV$^+$. The absorption band of the colored HV$^+$ species and PB appeared at around 600 nm (Fig. 8), and this overlapped well with the emission bands of the Eu(III) complex. Such overlap of the absorption and emission bands facilitates efficient FRET from the excited states of the Eu(III) complex to the ground states of HV$^+$. When the emission of the cell was monitored from the PB-modified-electrode side, the emission change was found to increase, probably because of the filtering effect of the colored PB film in addition to FRET from the

![Fig. 12. Changes in absorbance at 400, 500, 600 nm (top) and electrode potential (middle), and current response (bottom) of ITO/PB cell (path length was 10 mm) containing Eu(hfa)$_3$(TPPO)$_2$ and HV$_2^+$ in LiClO$_4$/PC solution.](image-url)
excited states of the Eu(III) complex to the ground states of HV$^{2+}$. Thus, the emission lifetime of the Eu(III) complex did not change in the ITO/PB cell without HV$^{2+}$ when emission was monitored from both the ITO side and colored PB-modified-electrode.

Finally, the stabilities of the switching between the emissive reflective modes were investigated. The changes in the absorption (600 nm) and emission (615 nm) of the ITO/PB cell under the sequential application of voltages of -0.8 V (10 s, coloring process) and 1.4 V (10 s, bleaching process) were monitored (Fig. 15). Under the application of -0.8 V, as the absorption band increased because of the EC reaction of HV$^{2+}$ and PB, the red emission of the Eu(III) complex was rapidly quenched within 5 s. After the voltage of 1.4 V was applied, the cell was completely bleached in 10 s. When the absorbance of HV$^{+}$ and colored PB decreased, the Eu(III) complex emission recovered to the initial intensity, indicating high reversibility of the emission-coloration switching. The absorbance of both the transparent and colored states of the cell was almost maintained after 250 cycles (Fig. 16), as was the emission intensity (Fig. 17).

Fig. 13. Emission spectra of the ITO/PB cell under the bias voltage of 1.4 V (10 s, red line) and -0.8 V (10 s, black dashed line), respectively. Inset: Photographs of the cell under dark condition when bias voltage of 1.4 V (10 s) and -0.8 V (10 s) were applied to the cell by irradiated of UV light (365 nm).

Fig. 14. Emission spectra of the ITO/PB cell without HV$^{2+}$ (red line; under bias voltage of 1.4 V (10 s), black dashed line: under bias voltage of -0.8 V (10 s)) under irradiation at 337 nm.

Fig. 15. Changes in the absorbance at 600 nm (blue dashed line) and emission intensity at 615 nm (red line) of the ITO/PB cell by applying the bias voltages of -0.8 V (10 s) and 1.4 V (10 s), respectively.

Fig. 16. Change in absorbance at 600 nm (top) and current (bottom) of ITO/PB cell by the stepping voltage at -0.8 V (10 s) and 1.4 V (10 s).
4. Conclusion

We successfully achieved electroswitching of photoluminescence and coloration with a quick response and high reversibility using a luminescent Eu(III) complex, an electrochromic molecule (HV\(^{2+}\)), and a PB-modified counter electrode for the HV\(^{2+}\) redox reaction. The switching voltage was reduced from -2.0 V to -0.8 V as a result of the stable redox reaction of PB. The response time and reversibility of the cell were also found to improve: in particular, coloring process was from 100 to 10 s, while bleaching process was from 600 to 10 s. The repetition stability of absorbance (600 nm) and emission intensity was maintained at initial value until 250 cycles. From the electrode potential measurements for ITO electrode as working and/or counter electrode and/or PB-modified electrode as counter electrode in ITO/ITO and ITO/PB cell, these improvements of electrochemical switching performance are likely to be a result of the low of voltage for coloration process and failure of solvent degradation, the well-balanced, and reversible electrochemical reaction of the ITO/PB cell, as well as the quantitatively balanced redox reaction of HV\(^{2+}\) and the PB film. We believe that the results of this research will contribute to the development of sensors and display devices such as monitors, digital signage, and e-paper.

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