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# Electroswitching of Emission and Coloration with Quick Response and High Reversibility in an Electrochemical Cell

Kenji Kanazawa, Kazuki Nakamura,\* and Norihisa Kobayashi\*[a]

Recently, materials with multifunctional response to external stimuli have attracted much attention because they can be used to develop chemical and biochemical sensors,<sup>[1]</sup> molecular logic gates<sup>[2]</sup> and memories,<sup>[3]</sup> and display devices.<sup>[4]</sup> Materials displaying both fluorescence and absorption switching have been reported. For example, the aggregation structure of a thermochromic system containing a fluoran dye and developer undergoes changes in response to thermal stimuli that are accompanied by color changes.<sup>[5]</sup> In this system, fluorescence on–off switching is induced by fluorescence resonance energy transfer (FRET) from a fluorescent dye to a colored fluoran dye. Photoresponsive multifunctional systems consisting of a photochromic diarylethene derivative associated with a fluorophore that exhibit both color and emission changes have also been reported.<sup>[4,6]</sup> In these systems, turn-on/turn-off fluorescence occurs; the initial fluorescent open-ring isomer is switched off during diarylethene photocyclization, and the closed-ring isomers are weakly fluorescent resulting from energy or electron transfer from the fluorophore to the closed-ring form of the diarylethene. The fluorescence can be readily restored through irradiation with visible light.

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.<sup>[7]</sup> Electrochromic 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,<sup>[8]</sup> smart windows,<sup>[9]</sup> dimming mirrors,<sup>[10]</sup> electrochromic 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<sup>III</sup> complex and an electrochemically active mate-

rial, diheptyl viologen (HV<sup>2+</sup>), have been integrated.<sup>[11]</sup> Generally, Eu<sup>III</sup> complexes have unique optical properties (line-like red emissions, long luminescence lifetimes, high transparency in the visible region (large Stokes shift), and high emission quantum efficiencies), which have resulted in their widespread application in phosphors, bioassays, and sensor development.<sup>[12]</sup> In the system developed by us, fluorescence switching was caused by FRET between the Eu<sup>III</sup> complex and HV<sup>2+</sup> in response to electrical stimuli.<sup>[11]</sup> Recently, it was shown that electroswitching of emission and coloration is possible when a photoluminescent material and an electrochemically active material are combined.<sup>[13]</sup> 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 is time-consuming (over 100 s), it is important to improve electroswitching performance.

Here, we report the electrochemical control of coloration and emission, with a quick response and high reversibility, for a novel electrochemical cell. Problems pertaining to responsiveness and reversibility in the case of our previous system were caused by the absence of counter electrode materials that could accelerate redox reactions of electrochromic materials. The cell reported here contains a luminescent Eu<sup>III</sup> complex (tris(hexafluoroacetylacetonato) europium-(III) bis(triphenylphosphine oxide): Eu(hfa)<sub>3</sub>(TPPO)<sub>2</sub>) and the electrochromic materials HV<sup>2+</sup> and Prussian blue (PB) (see Figure S1 for in the Supporting Information for chemical structures). PB is cyan in the oxidized state and colorless in the reduced state.<sup>[14]</sup> Thus, when HV<sup>2+</sup> 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<sup>2+</sup> and PB. Control of photoluminescence was also achieved as a result of HV<sup>2+</sup> and/or PB electrochromism via FRET from the excited states of Eu<sup>III</sup> ions to colored HV<sup>+</sup> and/or PB. In addition, the PB-modified electrode must act as a counter electrode for the HV<sup>2+</sup> redox reaction in order 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<sup>2+</sup>.

To investigate the electrochromic properties of the composite material, cyclic voltammograms (CVs) and changes in

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absorbance were measured (Figure S2 in the Supporting Information). The  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$  solution did not show an obvious reduction and oxidation in the measured potential range of 1.0–0.8 V (Figure S2a). For the  $\text{HV}^{2+}$  solution, one reductive peak and a corresponding oxidative peak were observed at potentials of –0.7 and –0.31 V, respectively (Figure S2b). As the reductive current increased from –0.4 V, the absorbance of the  $\text{HV}^{2+}$  solution at 400, 600, and 700 nm increased. On the basis of typical electrochromic behaviors of  $\text{HV}^{2+}$ , this observation is attributed to the absorbance of the reduced state of  $\text{HV}^{2+}$ .<sup>[15]</sup> On the other hand, reductive and oxidative peaks of the  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2/\text{HV}^{2+}$  solution were observed at –0.63 and –0.32 V (Figure S2c). As the reductive current increased from about –0.3 V, the absorbance at 400, 600, and 700 nm changed in a manner identical to that of the  $\text{HV}^{2+}$  solution. In the absorption spectrum of the colored  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2/\text{HV}^{2+}$  solution, new absorption bands observed at around 400 and 600 nm were in good agreement with those of the reduced  $\text{HV}^{2+}$  (Figure S3 in the Supporting Information). The coloration of  $\text{HV}^{2+}$  in the presence of the  $\text{Eu}^{\text{III}}$  complex is consistent with the typical electrochromic behavior of  $\text{HV}^{2+}$ ; thus,  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$  does not significantly affect the electrochromic behavior of  $\text{HV}^{2+}$ .

The electrochemical reactivity of the PB-modified electrode was analyzed in different solutions (Figure S4 in the Supporting Information). During a potential sweep from the negative to positive direction, the CV curve of the solution without  $\text{HV}^{2+}$  and the  $\text{Eu}^{\text{III}}$  complex displayed 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 (Figure S4a). In the absorption spectrum, a broad absorption band over 500 nm was observed (Figure S5 in the Supporting Information). These changes in absorbance are a result of the oxidation of PB. The electrochromic properties of the solutions containing the  $\text{Eu}^{\text{III}}$  complex,  $\text{HV}^{2+}$ , or  $\text{Eu}^{\text{III}}$  complex/ $\text{HV}^{2+}$  (Figure S4 in the Supporting Information) on the PB-modified electrode were very similar to those of the solution without  $\text{HV}^{2+}$  and the  $\text{Eu}^{\text{III}}$  complex, that is, the electrochemical reaction of  $\text{HV}^{2+}$  was not observed on the PB-modified electrode. These results suggest that the electrochemical reactivity of the PB-modified electrode was not affected by  $\text{HV}^{2+}$  or the  $\text{Eu}^{\text{III}}$  complex and that the conventional electrochromic reaction of PB (given below) occurred.

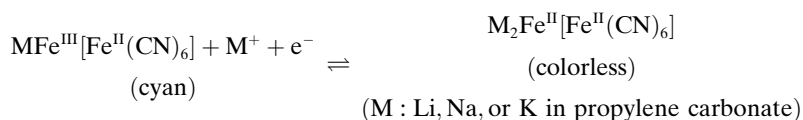


Figure 1 shows the absorption change at 600 nm and CVs of the ITO/ITO and ITO/PB cells (ITO, indium tin oxide). For the former cell, the absorbance at 600 nm increased from –1.75 V as the current increased because of the electrochemical reduction of  $\text{HV}^{2+}$ . On the other hand, a current flow in and coloration of the ITO/PB cell were observed

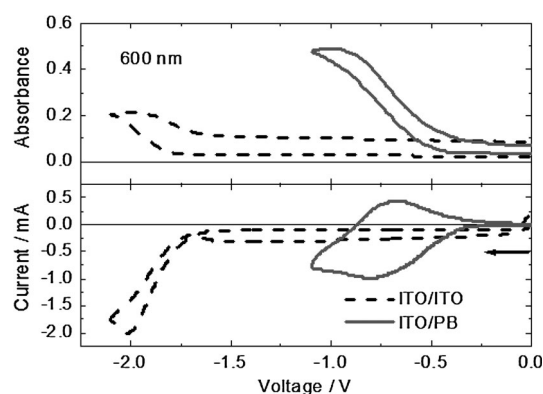


Figure 1. Change in absorbance at 600 nm (top) and CVs (bottom) of the ITO/ITO cell (dashed line) and the ITO/PB cell (solid line).

from –0.35 V, thus 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  $\text{HV}^{2+}$  redox reaction. In the ITO/ITO cell, because a suitable counter electrode material for the  $\text{HV}^{2+}$  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  $\text{HV}^{2+}$ . In the ITO/PB cell, oxidation of PB can accompany the reduction of  $\text{HV}^{2+}$ , thereby leading to an acceleration of  $\text{HV}^{2+}$  reduction in the cell. The lower oxidation potential of PB (about 0 V, Figure S4d in the Supporting Information) would be conducive to the coloration of the ITO/PB cell at a lower operation voltage compared to that of the ITO/ITO cell.

To investigate the coloration behavior of the ITO/PB cell, the absorption spectra of the cell were measured under the application of a bleaching voltage (1.4 V) and a coloring voltage (–0.8 V) (Figure 2). When the bias voltage of 1.4 V was applied for 10 seconds, no absorption bands were observed in the visible region (400–700 nm), indicating that the cell was colorless (see photo in Figure 2). By contrast, when the bias voltage of –0.8 V was applied for 10 seconds, the cell turned 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 ( $\text{HV}^+$ ) and the oxidized state of PB, suggesting that the color contrast of the cell could be improved by the co-coloration of  $\text{HV}^+$  and PB (Figure S6 in the Supporting Information).

In order to investigate the control of the emission, emission spectra of the ITO/PB cell were measured under the excitation of the hfa ligands (337 nm) for bias voltages of 1.4 and –0.8 V (Figure 3). The emission of the cell was monitored from the ITO electrode side. When the cell was in the transparent state (1.4 V), strong red emission bands of the  $\text{Eu}^{\text{III}}$  complex were observed at around 580, 590, 615, and 650 nm. These emission bands were attributed to the f–f transition  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J=0, 1,$

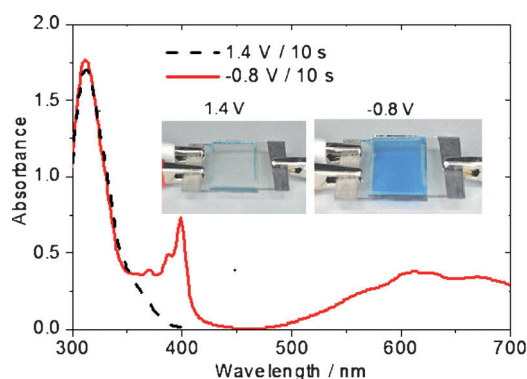


Figure 2. Absorption spectra of the cell under the bias voltages of 1.4 V (10 s, dashed line) and  $-0.8$  V (10 s, solid line), respectively). Inset: Photographs of the cell under bright conditions when bias voltages of 1.4 V (10 s) and  $-0.8$  V (10 s) were applied to the cell.

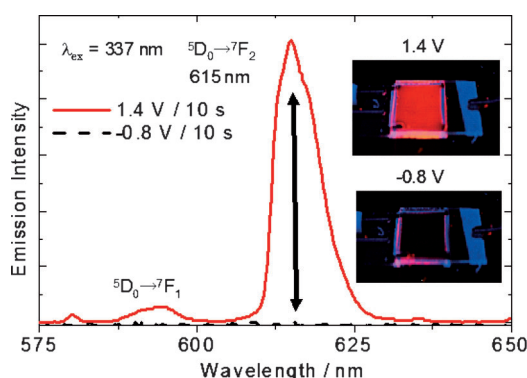


Figure 3. Emission spectra of the cell under the bias voltages of 1.4 V (10 s, solid line) and  $-0.8$  V (10 s, dashed line), respectively). Inset: Photographs of the cell under dark conditions when bias voltages of 1.4 V (10 s) and  $-0.8$  V (10 s) were applied to the cell under irradiation of UV light (365 nm).

2, and 3); this was considered as the “emission-on” state (see photo in Figure 3). When the cell was in the colored state ( $-0.8$  V), the red emission of the  $\text{Eu}^{\text{III}}$  complex was completely quenched, resulting in an “emission-off” state (see photo in Figure 3). In the case of the ITO/PB cell without  $\text{HV}^{2+}$ , the emission intensity of the  $\text{Eu}^{\text{III}}$  complex was not influenced by the application of a voltage (Figure S7 in the Supporting Information). Therefore, the quenching of the emission was caused by the colored  $\text{HV}^+$ . The absorption band of the colored  $\text{HV}^+$  species and PB appeared at around 600 nm (Figure 2) and overlapped well with the emission bands of the  $\text{Eu}^{\text{III}}$  complex. Such overlap of the absorption and emission bands facilitates efficient FRET from the excited states of the  $\text{Eu}^{\text{III}}$  complex to the ground states of  $\text{HV}^+$ .<sup>[8,15,16]</sup> When the emission of the cell was monitored from the PB-modified-electrode side, the change in emission was found to be increased, probably because of the filtering effect of the colored PB film in addition to FRET from the excited states of the  $\text{Eu}^{\text{III}}$  complex to the ground states of  $\text{HV}^+$ . Thus, the emission lifetime of the  $\text{Eu}^{\text{III}}$  complex did not change in the ITO/PB cell without  $\text{HV}^{2+}$  when the emis-

sion was monitored from both the ITO side and the colored PB-modified electrode.

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 (Figure 4). In the case of the former cell, the coloration process in the transparent state required the applica-

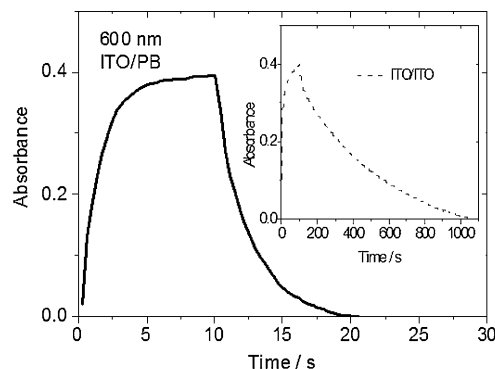


Figure 4. Chronoabsorptometric curves of the ITO/PB and ITO/ITO cells (inset) during the coloring and bleaching processes.

tion of  $-2.0$  V for 100 seconds to reach an absorbance of 0.4. The bleaching process required a longer time of 1000 seconds, even under short circuit. By contrast, coloration of the ITO/PB cell was achieved by application of  $-0.8$  V for 10 seconds, and bleaching was complete within 10 seconds under short circuit. 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 electrode.<sup>[17]</sup> The stable redox properties of the PB-modified electrode were responsible for the quantitatively balanced  $\text{HV}^{2+}$  redox reaction. Consequently, the coloration and bleaching rates of the ITO/PB cell improved. Finally, we investigated the stability of the switching between the emissive reflective modes. 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 (Figure 5). Under the application of  $-0.8$  V, as the absorption band increased because of the electrochromic reaction of  $\text{HV}^{2+}$  and PB, the red emission of the  $\text{Eu}^{\text{III}}$  complex was rapidly quenched within 5 seconds. After the voltage of 1.4 V was applied, the cell was completely bleached within 10 seconds. When the absorbance of  $\text{HV}^+$  and colored PB decreased, the  $\text{Eu}^{\text{III}}$  complex emission recovered to the initial intensity, thus indicating high reversibility of the emission-coloration switching. The switching behavior of the cell is shown in the movies provided as Supporting Information. The absorbance of both the transparent and colored states of the cell was nearly completely maintained after 250 cycles, as was the emission intensity (Figure S8 in the Supporting Information). These results indicate a high reversibility of the ITO/PB cell in comparison to the ITO/ITO cell, as a result of

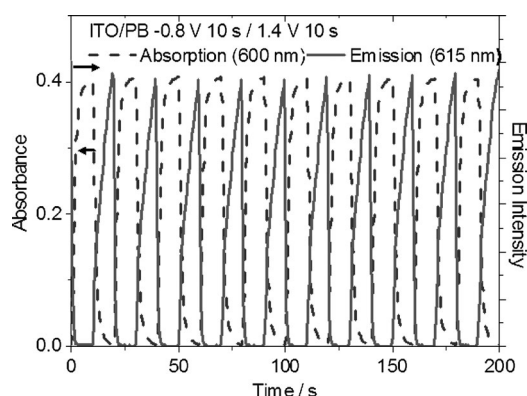


Figure 5. Changes in the absorbance (600 nm, dashed line) and emission intensity (615 nm, solid line) of the ITO/PB cell under the bias voltages of  $-0.8$  V (10 s) and  $1.4$  V (10 s), respectively.

a quantitatively balanced redox reaction of the PB that prevented the solution from undergoing an irreversible electrochemical reaction.

In summary, we successfully achieved electroswitching of emission and coloration with a quick response and high reversibility using a luminescent  $\text{Eu}^{\text{III}}$  complex, an electrochromic molecule ( $\text{HV}^{2+}$ ), and a PB-modified counter electrode for the  $\text{HV}^{2+}$  redox reaction. The switching voltage was reduced as a result of the stable redox reaction of PB. The response time and reversibility of the cell were also found to be improved. These improvements likely result from the well-balanced and reversible electrochemical reaction of the ITO/PB cell, as well as the quantitatively balanced redox reaction of  $\text{HV}^{2+}$  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.

## Experimental Section

The PB-modified electrode was prepared through electrochemical deposition on an ITO electrode (see the Supporting Information for experimental details). Details regarding the synthesis of  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ , experimental procedure, characterization data, electrochemical properties of materials, and cell structures are given in the Supporting Information.

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**Keywords:** electrochromism • energy transfer • europium(III) complex • luminescence • luminescence control

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