

# Dual emissive-reflective display materials with quick response and high reversibility using luminescent lanthanide (III) complex and EC materials

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## Abstract

An electroswitching device that enables modulation of both photoluminescence and coloration was obtained. The device consisted of luminescent lanthanide(III) complex  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$  (photoluminescence material) and an diheptyl viologen (electrochromic material). Coloration and emission control were achieved by only electrochemical reactions of  $\text{HV}^{2+}$ . 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. 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.

## 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 sensors, and display devices. 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. 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, smart windows, dimming mirrors, 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). 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 [1,2]. 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  $\text{HV}^{2+}$  (denoted as Eu(III)complex/ $\text{HV}^{2+}$ , see Fig. 1 for chemical structures) solution is time-consuming (over 100 s), it is important to improve electroswitching performance. These problems would be caused by absence of counter electrode reaction material against  $\text{HV}^{2+}$  redox. Therefore, oxidative reaction of supporting electrolyte, solvent and side reaction would occur at the anode during reductive reaction of  $\text{HV}^{2+}$ . This unfavorable oxidation was considered to be cause of degradation of DMD cell. The introduction of counter electrode material against  $\text{HV}^{2+}$  redox material would improve quick response and switching stability.

In this paper, we report the electrochemical control of coloration and emission, with a quick response and high reversibility, for a novel electrochemical cell. In order to achieve quick response and high switching stability of the cell, we introduced prussian blue (PB) modified electrode as a counter redox material against the  $\text{HV}^{2+}$  redox.

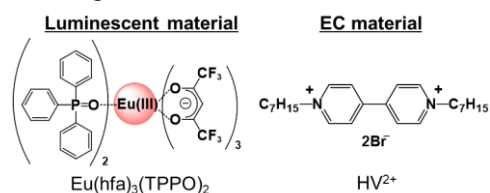


Fig. 1 Chemical structures of luminescent  $\text{Eu}^{3+}$  complex and  $\text{HV}^{2+}$ .

## 2. Experimental

The cell was constructed with ITO glass electrode and PB modified electrode (ITO/PB cell). The PC solution containing  $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$  (10 mmol/L),  $\text{HV}^{2+}$  (10 mmol/L), and  $\text{LiClO}_4$  (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  $\mu\text{m}$  by using plastic spacer (Lintec Co.). As the reference, the ITO/ITO cell with two ITO glasses electrodes was also fabricated.

### 3. Results and discussion

To investigate the electrochemical properties of the two-electrode cells (Fig. 2(a)), we measured the absorption change at 600 nm and CVs of the ITO/ITO and ITO/PB cells (Fig. 2(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  $HV^{2+}$ . 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.

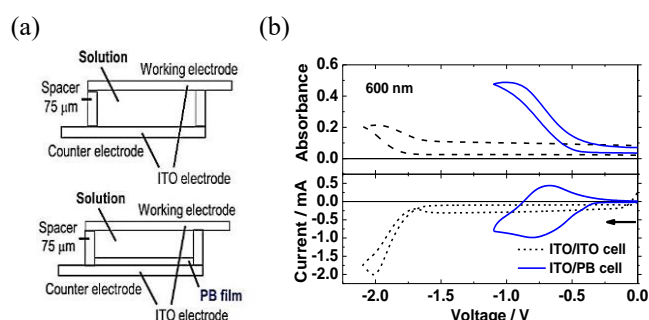


Fig. 2 (a) ITO/ITO (top) and ITO/PB (bottom) two-electrode cells. (b) Change in absorbance (top) at 600 nm and cyclic voltammograms (bottom) of ITO/ITO cell (black dashed line) and the ITO/PB cell (blue line) containing  $HV^{2+}$  and  $Eu(hfa)_3(TPPO)_2$  in  $LiClO_4/PC$  solution.

Fig. 2 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. 2). 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.

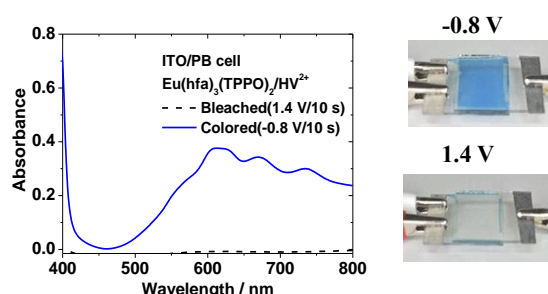


Fig. 3 Absorption spectra of the ITO/PB cell (under bias voltage of 1.4 V (10 s) and -0.8 V (10 s) for the black dashed and blue lines, respectively) containing  $HV^{2+}$  and  $Eu(hfa)_3(TPPO)_2$  in  $LiClO_4/PC$  solution.

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. 4). When the cell was in the colored state (-0.8 V), the red emission of the  $Eu(III)$  complex was completely quenched (photo in Fig. 4). 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. 3), 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  $HV^{+}$ . Additionally, the response time, switching stability of both coloration and bleaching in the cell were also improved due to quantitatively balanced reaction of the  $HV^{2+}$  and PB film.

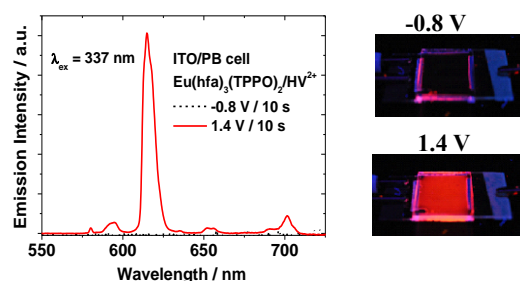


Fig. 4 Emission spectra of the ITO/PB cell under the bias voltage of 1.4 V (10 s, red line) and -0.8 V (10 s, black dashed line), respectively. Inset: Photographs of the cell under dark condition when bias voltage of 1.4 V (10 s) and -0.8 V (10 s) were applied to the cell by irradiated of UV light (365 nm)

### 3. Conclusions

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.

### Acknowledgements

This research was partly supported by JSPS KAKENHI Grant Number 15K05660 and 23750208 from the Japan Society for the Promotion of Science (JSPS), Iketani Science and Technology Foundation, Ogasawara Science and Technology Foundation, and JSPS Research Fellowships for Young Scientists (No. 13J07191).

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