

# Luminescence Color Control Based on Electrochromic Reaction Using Luminescent Leuco Dye Derivatives

**Kazuki Nakamura, Namiko Yanagawa, and Norihisa Kobayashi**

Corresponding author's Nakamura.Kazuki@faculty.chiba-u.jp

Graduate School of Chiba University

Keywords: Electrochromism, Leuco dye, Luminescence control, Energy transfer

## ABSTRACT

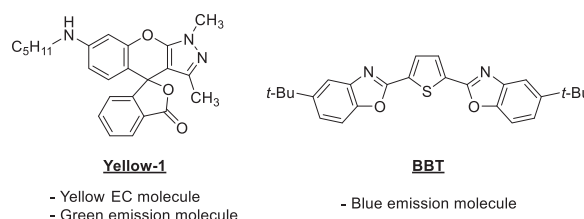
We have reported photo-and electrochemical-functional materials enabling the dual reflective and emissive function by combining electrochromic materials and luminescent materials. In this study, for achieving electrochemical control of luminescence color, we combined various functional molecules such as electrochromic molecules, luminescent molecules. As a result, luminescence colors were successfully controlled through inter-molecular energy transfer between luminescent molecules and electrochromic molecules.

## 1 INTRODUCTION

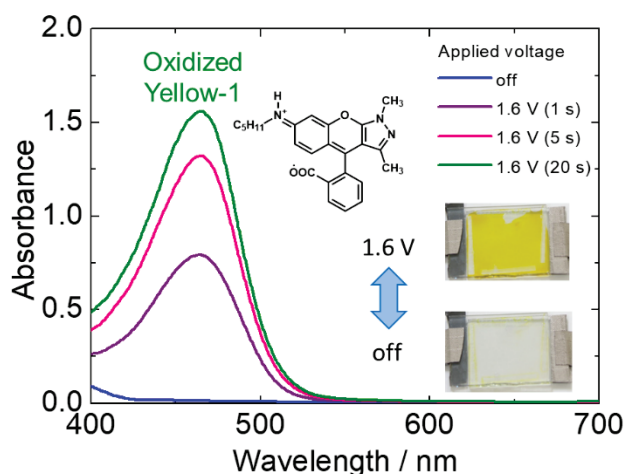
Electrochromic (EC) materials can change their optical states reversibly by electrochemical redox reaction. We have already reported photo- and electrochemical-functional materials enabling dual reflective and emissive function by combining EC materials and luminescent lanthanide(III) complex.<sup>[1,2]</sup> This modulation of emission is caused by control of photoexcitation energy transfer from the luminescent lanthanide(III) complex to EC material.<sup>[3]</sup> In this study, for achieving electrochemical modulation of luminescence color, we investigated electrochemical and photophysical properties of the hybrid materials including a functional leuco dye which shows yellow coloration and green emission by electrochemical oxidation and organic blue luminescent molecule.

## 2 EXPERIMENT

The solution was prepared by dissolving the 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBT) (1 mmol/L) as blue emitter, and fluoran molecule (Yellow-1) which shows yellow coloration and green luminescence under oxidized state (80 mmol/L) in propylene carbonate. The chemical structures of the photo functional molecules are shown in Fig. 1. This solution placed between two ITO electrodes through a 75  $\mu\text{m}$  spacer to construct a two-electrode electrochemical cell. For this device, absorption, emission (excitation wavelength 360 nm), and emission lifetime measurement (excitation wavelength 360 nm) were performed before and after application of coloration voltage of Yellow-1 molecule (1.6 V).



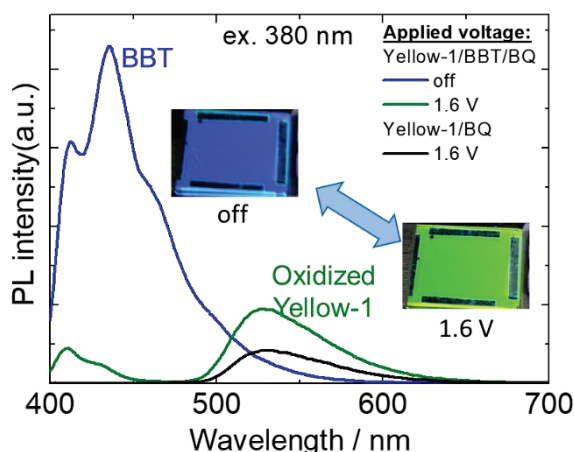
**Fig. 1 Chemical structures of the EC molecule and luminescent molecule.**



**Fig. 2 Change of absorption spectra of the electrochemical cell during voltage application.**

## 3 DISCUSSION

We first studied the optical characteristics of the electrochemical cell before and after applying the coloring voltage of Yellow-1. Fig. 2 shows the absorption spectra and the photographs of the cell. When coloration voltage was not applied, the cell was colorless and transparent with no absorption in the visible wavelength range. When the coloration voltage of 1.6 V was applied to the cell, a new absorption band at around 430 nm appeared and the color turned bright yellow. This absorption change is induced by electrochemical oxidation of Yellow-1.



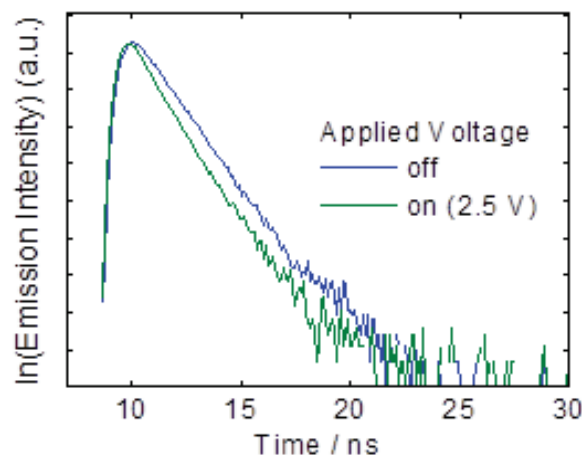
**Fig. 3** Change of photo-luminescence spectra of the electrochemical cells during voltage application.

Next, we investigated the change of luminescence characteristics of the cell. Fig. 3 shows the emission spectra and photographs of the cell under excitation light (360 nm). Before applying voltage, blue fluorescence from BBT at around 435 nm was observed. When coloration voltage of Yellow-1 was applied, the fluorescence from BBT greatly decreased. After oxidation of Yellow-1, a new emission band appeared at 530 nm and luminescence color changed to green. This new emission band is caused by Yellow-1 molecule at electrochemically oxidized state.<sup>[4,5]</sup> In this way, luminescence color of mixture solution of BBT and Yellow-1 can be modulated by electrochemical redox reaction of Yellow-1.

Finally, the mechanism of emission color control was discussed in detail. The luminescence lifetime of the BBT in the electrochemical cell was measured before and after applying the coloration voltage. The emission lifetime of BBT before voltage application was found to be 1.19 ns, and the lifetime shortened to 1.02 ns under application of coloration voltage. Efficiency of excited energy transfer from BBT to colored Yellow-1 was calculated to be approximately 14 %. Moreover, luminescent intensity of colored Yellow-1 increased by the presence of BBT. These results indicated that energy transfer occurred from BBT to colored Yellow-1.

#### 4 CONCLUSIONS

In summary, we reported electrochemical control of luminescent color from blue to green using organic luminescent material and leuco dye. The emission color change was induced by both excited energy transfer and absorption of BBT emission.



**Fig. 4** Emission life time (435 nm) of BBT / Yellow-1 mixture solution in two-electrode cell (blue line: under open circuit condition, green line: the application of electrical voltage).

#### REFERENCES

- [1] K. Nakamura, K. Kanazawa, and N. Kobayashi, "Electrochemically controllable emission and coloration by using europium (III) complex and viologen derivatives," *ChemCommun*, Vol. 47 No. 36, pp. 10064-10066 (2011).
- [2] K. Nakamura, K. Kanazawa, and N. Kobayashi, "Electrochemically-switchable emission and absorption by using luminescent Lanthanide(III) complex and electrochromic molecule toward novel display device with dual emissive and reflective mode," *Displays*, Vol. 34, No. 5, pp. 389-395 (2013).
- [3] K. Kanazawa, Y. Komiya, K. Nakamura, and N. Kobayashi, "Red luminescence control of Eu(III) complexes by utilizing the multi-colored electrochromism of viologen derivatives," *Phys. Chem. Chem. Phys.*, Vol. 19, pp. 16979-16988 (2017).
- [4] K. Kanazawa, K. Nakamura, and N. Kobayashi, "High-contrast electroswitching of emission and coloration based on single-molecular fluoran derivatives," *J. Phys. Chem. A*, Vol. 118, No. 31, pp. 6026-6033 (2014).
- [5] K. Kanazawa, K. Nakamura, and N. Kobayashi, "Electroswitchable optical device enabling both luminescence and coloration control consisted of fluoran dye and 1,4-benzoquinone," *Sol. Energy Mater. Sol. Cells*, Vol. 145, pp. 42-53 (2016).