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Electrofluorochromic Device Based on a Redox-Active Europium (III) Complex

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ABSTRACT

Electrofluorochromism owing to redox reactions on the center europium (Eu) ion in ionic liquids is examined for the helicate complexes (abbreviated to EuL) with hexadentate pyridine derivative. Typical electrofluorochromism requires extra electroactive units complementing intra- or intermolecular energy transfer to quench fluorophores. Herein, an unprecedentedly simplified electrofluorochromic system overcoming such issues is demonstrated by utilizing reversible electrochemistry of EuL between Eu^{3+} and Eu^{2+} , which accompanies large emission transition. A three-electrode electrochemical switching device is facilely prepared with an ionic liquid $[\text{BMIM}][\text{PF}_6]$ and EuL mixture. Benefiting from the

stable helical coordinated structure of the ligand in [BMIM][PF₆], highly enhanced red fluorescence of EuL with small quantity (≤ 1 wt%) is utilized. Rapid response and large contrast of luminescence are achieved: the emission is drastically quenched at the reduced state (Eu²⁺) and it is successfully restored by subsequent oxidation (Eu³⁺). The reversible fluctuation of excitation and emission spectra of an electrofluorochromic device is achieved in the potential window within ± 2 V. The device affords excellent optoelectric properties in terms of well-controlled luminescence switching depending on the applied potentials and its durability. This work paves an efficient and smart way toward Eu luminescence control in the optoelectronic devices.

1. INTRODUCTION

Reversible optical switching by electrical tuning of the molecular energy state has been much of interest recently because of their great potential in optical memories,¹⁻³ displays,⁴⁻⁶ sensors,⁷ or information encryption.^{8,9} To meet the demands, electrochemically driven luminescence switching based on electrofluorochromic molecules which change their fluorescence depending on their redox state attracts significant attention.⁸⁻¹⁴ Among the fluorophores enabling such luminescence switching systems, lanthanide complexes arise as one of the particularly attractive candidates.^{15,16} Because they can offer sharp, well-defined characteristic fingerprint emission bands and long-lived luminescence at visible and near-infrared regions, those aspects are rarely achieved with organic dyes.^{17,18} Therefore, external stimuli such as light, electrical, thermal and chemical sources have been attempted to modulate the luminescence.^{15,16,19,20}

The direct electrochemical redox reaction of the center Eu ion in complexes with various ligand systems has been reported including cryptates,²¹ polyoxodiaza cryptands,²² polyazacryptands,^{23,24} macrocyclic or linear poly(aminocarboxylates)-type ligands,²⁵⁻²⁷ and a Eu-encrypted Preyssler anion.²⁸ With the exception of cryptates and the Eu-encrypted

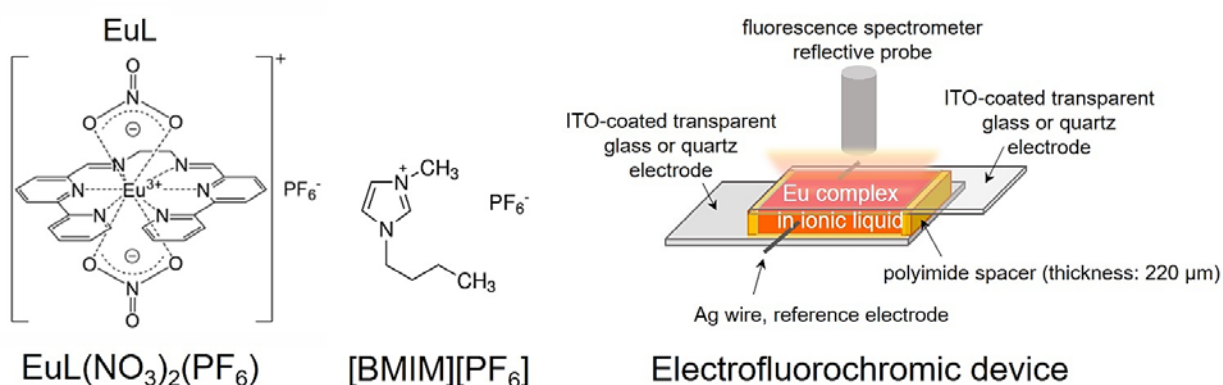
Preyssler anion, the resulting complexes of macrocyclic and linear ligands showed much negative redox potentials relative to the $\text{Eu}^{3+/2+}$ aqua ion (-585 mV vs. Ag/AgCl).^{22,27} In particular, none of those Eu complexes reported the $\text{Eu}^{3+/2+}$ electrochemistry-driven luminescence control.

To afford electrofluorochromism from Eu complexes, strategies engineering energy-transfer to fluorophores *via* redox state control of coordinated ligands or other electroactive species have been mostly reported.²⁹⁻³⁵ For example, emission was switched by the redox reaction of the covalently linked electroactive units, such as ferrocene moiety in a dyad form^{29,30} or a triarylamine-based ligand.^{31,32} On the other hand, facilitating intermolecular electron transfer between the Eu complex and electroactive species has been reported by additionally introducing electrochromic molecules such as viologen derivatives^{33,34} or the TiO_2 electrode adsorbed with the Eu complex.³⁵ These studies reported fair response and reversibility of the luminescence switching by facilitating the redox process. Nevertheless, to guarantee practical and long-term applications, it would be much advantageous to directly tune the metal ion of Eu complex electrochemically and its interplay with luminescence switching which provides considerable opportunities in the field of electrofluorochromic devices. However, the cases where the single moiety acts both as the light emitter and the redox switch are much scarce.

Chemical reduction of Eu^{3+} yielding Eu^{2+} commonly undergoes in harsh conditions such as heating for several hours at very high temperature around 1000-1300 °C for sintering in a thermal ($\text{H}_2 + \text{N}_2$)-reducing atmosphere.^{19,36,37} Recently, Ishii and Hasegawa reported on the novel Eu^{3+} complex enabling facile chemical reduction to Eu^{2+} .^{38,39} By thermally activated interfacial reduction of the Eu complex on SiO_2 nanoparticles, they could facilely attain f-f to f-d transition emission to quench Eu^{3+} signature red-emitting peaks achieving the blue-emitting Eu^{2+} state.³⁸ In addition, the complex (EuL) shown in scheme1 was designed using hexadentate ligands based on the chelate effect for the high molecular stability.^{40,41} The

helicated ligands are energy donors and they can act efficiently keeping the coordination with the Eu ion.⁴⁰⁻⁴³ The authors revealed that the molecular stability of EuL in a viscous medium such as an ionic liquid could suppress the molecular fluctuations in the ligands; thus, energy transfer is enhanced resulting in the much higher quantum yield than that in the organic solvent.⁴⁰ Based on those intriguing characteristics of EuL, we anticipated that electrochemical reduction would be possible to quench the strong red emission from EuL in the support of the ionic liquid. To the best of our knowledge, there has never been a challenge for the electrochemical luminescence switching based on the intrinsic redox property of the center Eu ion which requires no complementary electroactive unit to facilitate energy transfer to quench Eu emission.

We describe here the first example of an electrofluorochromic device exhibiting electrochemically triggered direct switching of the center europium ion between Eu^{3+} and Eu^{2+} accompanying luminescence of the emissive and quenched state, respectively. Highly enhanced red emission of EuL in an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (abbreviated as [BMIM][PF₆]) was switched on and off remarkably upon application of potentials for different redox states. The current work showcases a highly transparent and colorless device with large transitions in emission which can be a promising candidate for multistage encrypted information processing and displays.



Scheme 1. Molecular structures of the Eu complex (EuL) and the ionic liquid [BMIM][PF₆], and the structure of the three-electrode electrofluorochromic device and a reflective probe for electrochemically controlled fluorescence switching detection.

2. RESULTS AND DISCUSSION

Scheme 1 describes molecular structures of the utilized EuL and [BMIM][PF₆], and the schematics of the three-electrode electrofluorochromic device. The blend of EuL (0.5-1 wt%) and [BMIM][PF₆] was introduced to the device sealed by polyimide tape spacers. The effective fluorophore concentration was much less than other fluorophore-based electrofluorochromic devices because of the stable coordination structure of the EuL in [BMIM][PF₆].

First, the HOMO-LUMO band gap energy and electrochemical properties of EuL were characterized. The optical band gap ($E_g = 1240/\lambda_{\text{onset, abs}}$) of EuL was determined as 3.48 eV based on the UV-visible absorption spectrum.⁴¹ Cyclic voltammogram (CV) of EuL in acetonitrile solution (Figure S1a) revealed the reduction and oxidation potentials positioned at -0.36 V and +1.20 V (vs Ag/AgCl), respectively. As the reduction potentials to form Eu²⁺ ion in complexes with ligands such as polyoxodiaza cryptands,²² polyazacryptands,²⁴ macrocyclic or linear poly(aminocarboxylates)-type ligands²⁵⁻²⁷ were in the range of -1.4 V to -0.7 V (vs. Ag/AgCl) in the several previous studies, more positively shifted reduction potential of EuL at -0.36 V was probably benefited from electron-donating oligo-pyridine ligand.^{21,44,45} The large difference ($\Delta E \sim 840$ mV) between the oxidation and reduction peak suggests that this reaction is not a completely reversible electron transfer, but the Eu ions certainly showed electrochemical redox response repeatedly. The linear relationship of the square root of the scan rate and the corresponding anodic/cathodic peak current (Figure S1b) revealed that the electrochemical reaction of EuL was governed by the diffusion of Eu ion in

the electrolyte medium. E_{LUMO} was determined as -4.27 eV from reduction onset potential, and the E_{HOMO} value of -7.75 eV was calculated from the equation $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}$. As shown from the CV upon voltage scanning between -1.2 V and +2.0 V at 20 mV/s in Figure 1a, the redox potentials of EuL (1 wt%) in [BMIM][PF₆] in the three-electrode device (scheme 1) were observed at around -0.66 and +1.80 V (vs Ag wire). In comparison with that measured from the CV in acetonitrile solution (Figure S1a), shift and the large peak separation upon re-oxidation might come from the ohmic drop in the cell and slow down the electrochemical process occurring at the counter electrode. Nevertheless, europium ions exhibited reproducible redox peak positions and current upon repeated cycles without any degradation implying the stable coordinated states of Eu³⁺ and Eu²⁺.

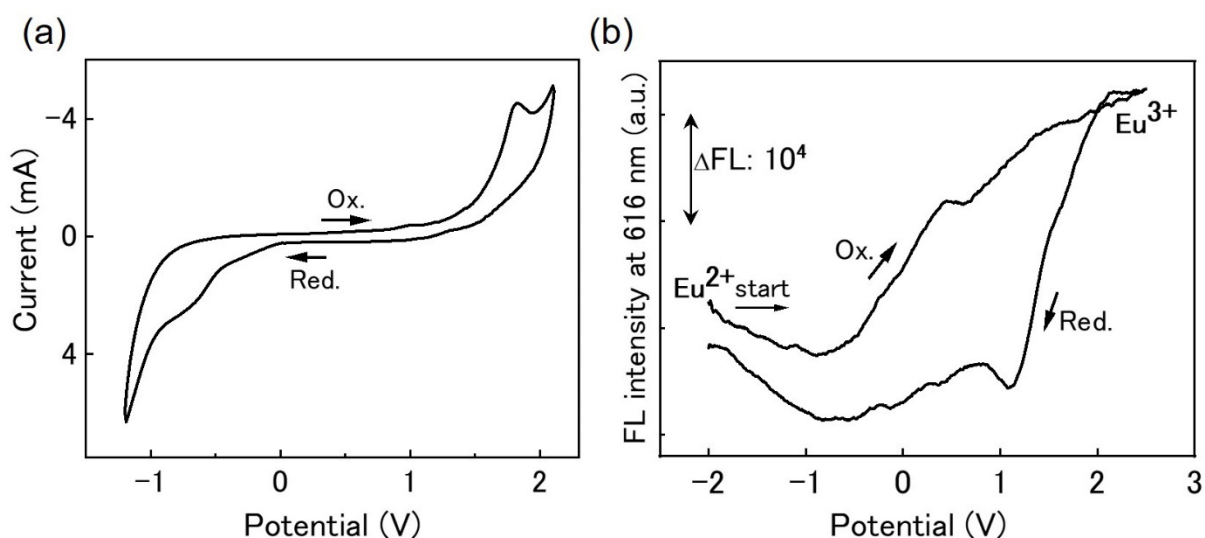


Figure 1. (a) Cyclic voltammogram of EuL (1 wt%) dissolved in [BMIM][PF₆] in a three-electrode switching device based on two ITO glass substrates and an Ag wire reference and (b) the emission intensity transition monitored at 616 nm upon starting from the Eu²⁺ state.

Simultaneously, we monitored the emission intensity of the device at 616 nm in which we presumed that the intrinsic red emission from Eu would be affected by the redox reaction of the fluorophore. Surprisingly, as shown in Figure 1b, the fluorescence intensity curve has

decent consistency with the current change during CV (Figure 1a). It showed a gradual increase in the emission intensity upon oxidative scanning starting from the reduced Eu^{2+} state at -2.0 V and then almost saturated from +1.5 V by reaching Eu^{3+} -rich state. Besides, the reversed potential to the negative direction drastically reduced the emission intensity and its minimum reached around -0.8 V which is close to the reduction potential of Eu^{3+} . Therefore, this cohesive optical behavior can be considered to be electrochemically triggered emission caused by the redox-active EuL.

To specify how the electrochemical reaction of $\text{Eu}^{3+}/\text{Eu}^{2+}$ influences the optical behavior of the Eu complex, we examined the excitation and emission spectra of the device depending on the applied potential as shown in Figure 2. Prior to the investigation, we checked the luminescence spectra of ITO glass and ITO quartz electrodes and [BMIM][PF₆] exhibiting inappreciable emission (Figure S2). The initial (before voltage application) state of the cell exhibits sharp emission originating from the f-f transitions of Eu^{3+} at 580, 592, 616, 649, and 686 nm assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively ($\lambda_{\text{ex}} = 330$ nm). The spectrum well-corresponds to ones confirming a coordination structure of EuL in acetonitrile and in [BMIM][PF₆].^{40,41,46} A series of luminescence spectra (Figure 2b) was measured by applying negative potentials of -0.7, -1.5, and -2.0 V for 1 min each. Increasing negative potential resulted in a gradual decrease in emission intensity in a whole emission region 580, 592, 616, 649, and 686 nm because of the reduction of Eu^{3+} species to negligible weakly emissive Eu^{2+} which contributes to f-f transitions and f-d transitions, respectively. At -2.0 V, almost 80% decrease in the original emission intensity (ON/OFF ratio of 5.6) was witnessed at 616 nm. This optical contrast is larger than those observed from ferrocene-Europium dyad (ON/OFF ratio of around 1.5),^{29,30} and comparable to those from Eu coordinated with triarylamine-based ligands as redox-active centers (around 85% decrease).^{31,32}

Afterward, upon applying positive potentials at +1.0, +1.5, and +2.0 V for 1 min each, the distinctive restore of the emission spectra especially at 580, 592, 616, 649, and 686 nm was observed. Consequently, 70% of the quenched emission was restored at +1.5 V. Although luminescence was further quenched by widening the potential window to -2.5 V, neither the restore of the emission nor the rise of anodic current was observed during the re-oxidation process which can be ascribed to the decomposition of metal coordinates or generation of irreversible reduced species. This implies that the reversible redox process between Eu^{2+} (weak emission) and Eu^{3+} (strong emission) and electroactive species are retained within ± 2 V.

Meanwhile, the excitation spectrum (Figure 2a) corresponding to each luminescence spectrum was monitored at 616 nm in which the f-f emission band reflects the $\pi\text{-}\pi^*$ transition of the ligand. At the initial state (voltage off, Eu^{3+}), the band was centered at 335 nm accompanying a subtle trace of a band evolution around 315 nm assignable to the $\pi\text{-}\pi^*$ transition of the ligand. Upon the reduction process with negative potentials, a distinctive tendency of band sharpening accompanying intensity decrement around 315 nm was observed. In the most reduced state at -2.0 V, the excitation band showed largely deficient intensity in the short wavelength region. Upon subsequent oxidation, the excitation band exhibited re-emergence of the band around 315 nm again.

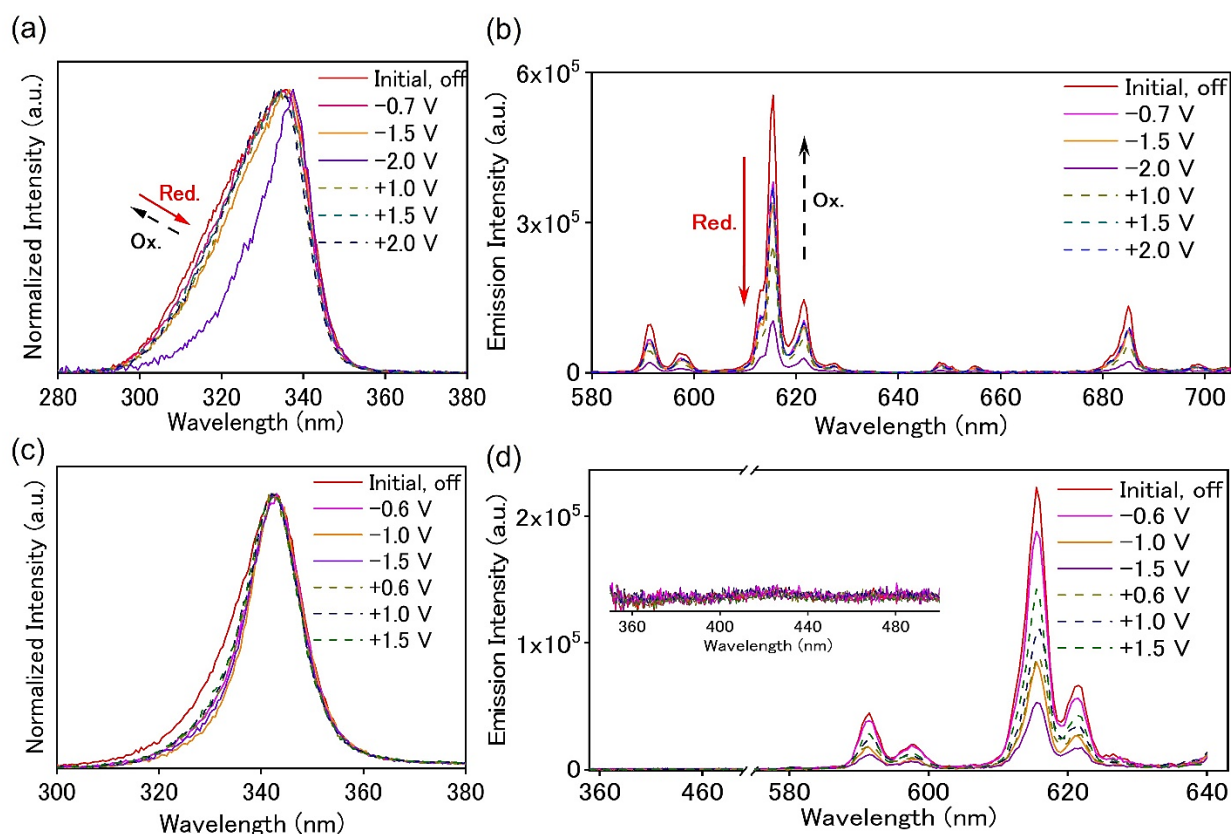


Figure 2. Excitation and luminescence spectra of the devices at different applied potentials ($\lambda_{\text{mon}} = 616 \text{ nm}$, $\lambda_{\text{ex}} = 330 \text{ nm}$). A Device based on ITO glass electrodes containing EuL (1 wt%) in [BMIM][PF₆]: (a) excitation and (b) luminescence spectra. A device based on ITO quartz electrodes containing EuL (0.5 wt%) in [BMIM][PF₆]: (c) excitation and (d) luminescence spectra. Inset of (d) shows the spectral change in the blue emissive region.

Furthermore, optical measurement carried out with a device based on ITO-coated quartz electrodes allowed us to rule out the luminescence contribution from the glass substrate of the device. Eventually, identical optical transition observed with the ITO glass electrode-based device was reproducible for both excitation (Figure 2c) and luminescence (Figure 2d) spectra depending on the applied voltages. In particular, compared with the drastic transition observed for red emission, expected blue emission from the f-d transition³⁸ of Eu²⁺ species in the range of 400-500 nm (inset of Figure 2d) was hard to distinguish because of its intrinsic weak emission and overlap with the emission band from the quartz electrode (Figure S2b).

Anyhow, the reversible electrochemistry of Eu^{2+} species confirmed from CV clearly supports that it is the origin of the EuL switching to another state, not originated from the redox reaction of organic ligands or $[\text{BMIM}][\text{PF}_6]$.

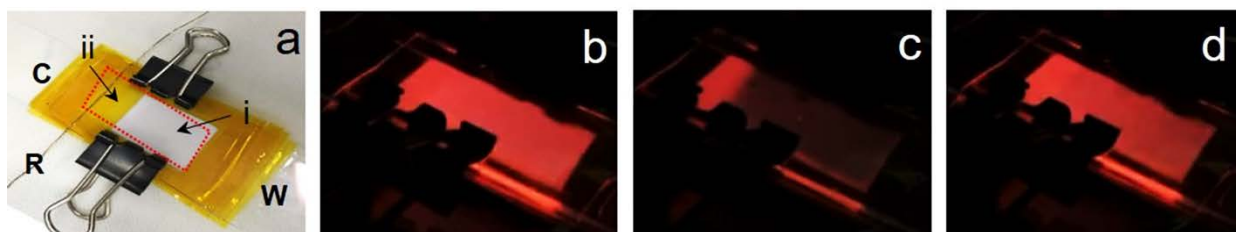


Figure 3. (a) Image of a switching device under room light consisting of topside working (W), backside counter (C), and reference (R) electrodes. A mixture of EuL and $[\text{BMIM}][\text{PF}_6]$ locates between two electrodes isolated by yellow polyimide tapes: (i) emission on/off switching area; (ii) partially insulating area (C is masked with polyimide tape); thus, the viewed emission is always “ON”. (b-d) Images of the device under a 365 nm handheld UV lamp during the fluorescence switching at different potentials applying 5 s each: (b) initial state (0 V, Eu^{3+} state), (c) reduced state (-1.8 V, Eu^{2+} state), and (d) re-oxidized state (+2.0 V, Eu^{3+} state).

Figure 3 shows a series of pictures showing the fluorescence of the device as a function of the applied electrochemical potentials. Surprisingly, clear on-off switching of fluorescence was visible by our naked eyes. A colorless and transparent cell (Figure 3a) fluoresce red under a 365 nm UV lamp at the beginning (b) and it becomes dark with low emission when a negative potential is applied. The emission is almost extinguished when the applied potential is -1.8 V (c), whereas the fluorescence is restored on the return sweep at +2.0 V (d). Simultaneous fluorescence on-off contrast is well visualized between the conductive area (i) and insulating nonresponsive area (ii). Effective quenching in Eu^{2+} -rich-(i) and its subsequent restoring to the almost same emission intensity indicates the efficient fluorescence switching which originates from the highly reversible electrochemical reduction (Eu^{2+}) and reoxidation (Eu^{3+}) process of the Eu complex in the device.

Such an electrofluorochromic switching was durable upon repetitive cycling between the oxidative and reductive potentials, as shown in Figure 4. Versatile control of emission contrast could be achieved by changing the potentials stepwise (Figure 4a), and -1.8 and +2.0 V turned out to be an optimized condition to achieve both stable and the largest contrast. At the fluorescence switching time test (Figure 4b), the device exhibited the almost same fluorescence contrast for switching times of 30 and 10 s which means full redox transition completes within 10 s. At the shorter switching time of 5 s, although the emission contrast decreased to 40%, still clear and stable switching behavior was observed with a consistent ON/OFF ratio of around 2.2. The average response time estimated at 90% of the full switch was 7 and 2 s for the quenching and recovering process, respectively. Besides, even after 100 cycles of switching (+2.0 and -1.8 V for 30 s/step), the device showed stable and reversible response with consistent fluorescence contrast, as observed from Figure 4c, indicating the device has durability for 100 cycles. The largest emission switching of europium(III) complex-based device was reported as 1/3000 contrast in 210 s with $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ and an electrochromic diheptyl viologen blend system.³³ However, different from our system, the luminescence of the Eu(III) complex was quenched indirectly by the electrochemical coloration of diheptyl viologen *via* intermolecular energy transfer mechanisms. In addition, the emission control from OFF to ON state was not electric field-driven but by the gradual conversion of viologen derivatives from the radical cation to dication at the open-circuit state by 15 min which is quite slow.³³ Meanwhile, in terms of switching response and durability, Eu complex-adsorbed TiO_2 electrode in the liquid electrolyte showed the most rapid response so far exhibiting 1 s for quenching and 3 s for recovery with the switching consistency of 50 cycles.³⁵ This indicates that our device has a fast response considering its viscous electrolyte medium and performs well with superior durability. As described above, the well-controlled electrochemical switching from Eu^{3+} to Eu^{2+} accompanying red luminescence “ON” and

“OFF” state was successfully utilized for the electrofluorochromic device. Reversible emission transition upon electrochemical reduction and oxidation of the Eu ion exploited in this study is summarized in Figure S3. Stable emission switching along with decreased redox potentials is attributed to the chelate effect of oligo-pyridine moieties bearing the stable coordination mode which act as efficient energy donors.⁴⁶

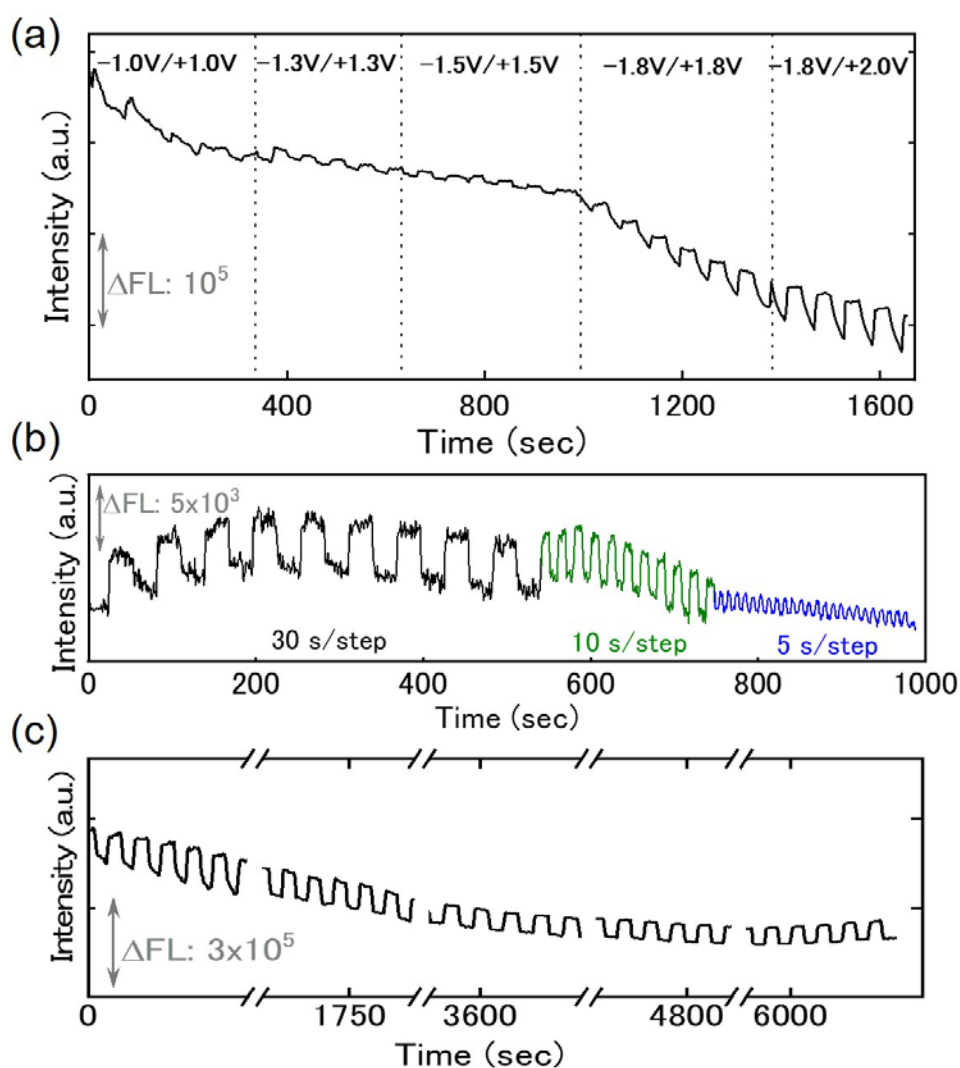


Figure 4. Fluorescence switching responses of the ITO quartz-based device monitored at 616 nm (a) under different applied potentials of -1.0 to +1.0 V, -1.3 to +1.3 V, -1.5 to +1.5 V, -1.8 to +1.8 V and -1.8 to +2.0 V, (b) under applied step potential of -1.8 to +2.0 V with a step duration time for 30, 10, and 5 s at each potential. (c) Durability test on fluorescence switching over 100 cycles upon applied potential of +2.0 and -1.8 V for 30 s per each step.

3. CONCLUSION

In summary, we have successfully developed ON/OFF switching of the luminescent europium complex based on its intrinsic redox properties of the metal ion in the electrochemical device for the first time. It provided a remarkably facile way to control the intense red luminescence of Eu^{3+} by electrochemical reduction to weakly emissive Eu^{2+} and to turn on the luminescence reversibly upon oxidation by the moderate potential application. Versatile electrochemical switching properties and the highly transparent and colorless device would pave its great potential for encrypted information processing and displays.

EXPERIMENTAL SECTION

Materials: EuL ($[\text{Eu}(\text{L})(\text{NO}_3)_2](\text{PF}_6)$) was synthesized according to the reported procedure.⁴¹ [BMIM][PF₆] (1-butyl-3-methylimidazolium hexafluorophosphate), anhydrous electrochemistry grade acetonitrile and tetrabutylammonium perchlorate (TBAP) were purchased from TCI Japan and utilized without further purification. Ag wire was purchased from Miwa Metal Co. ITO coated quartz electrode ($10 \text{ } \Omega \text{ sq}^{-1}$) was purchased from Alliance Biosystems Inc. and cleaned before use with a detergent, deionized water and acetone in an ultrasonic bath.

Preparation of Electrofluorochromic cells: A blend of EuL and the ionic liquid was prepared by dissolving EuL into [BMIM][PF₆] at 0.5 or 1 wt% concentration upon vigorous stirring and nitrogen gas purging. As shown in scheme1, the three-electrodes electrofluorochromic device was fabricated by two transparent ITO coated glass or quartz substrate as working and counter electrodes (electrode area $\sim 2 \text{ cm}^2$) which were separated by polyimide tape spacers (220 μm thick) and a silver wire placed as reference electrode between the two electrodes.¹³ The EuL mixture was injected into the device and the

sandwiched substrate edges were fixed by clips to prevent the leakage of the EuL blends from the device.

Measurements: The electrochemical measurements were made with a universal potentiostat (model ALS604EZ (BAS Inc.)). CV of EuL (1.2 mM) in acetonitrile electrolyte solution (TBAP, 0.1M) was investigated with platinum disk (W), platinum wire (C) and Ag/AgCl reference electrode. CV of EuL (1 wt%) and [BMIM][PF₆] blend was measured in the electrofluorochromic cell described in Scheme 1 and Figure 3a. A scan rate of 20 mVs⁻¹ was used for CV measurements. All excitation and luminescence spectra were measured using Horiba Jobin-Yvon Fluorolog 3-22. Y-50 filter was used for excitation spectra measurement. UV cut filter was introduced in case of luminescence spectra recording of ITO glass electrode-based device. In-situ luminescence transition of the electrofluorochromic cell upon electrical potentials was monitored using Horiba Jobin-Yvon Fluorolog 3-22 equipped with an order-made reflective probe and stage, and cyclic voltammogram or chronocoulometry of the potentiostat. During the measurement, the working electrode side of the device faced the reflective probe of the luminescence spectrometer for electrochemically controlled fluorescence switching detection as shown in Scheme1. The ON/OFF ratio of the optical contrast was determined by dividing the ON-state emission intensity with the OFF-state intensity.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Cyclic voltammogram of EuL (1.2 mM) in acetonitrile electrolyte solution (TBAP, 0.1M). The plotting result of the square root of scan rate and corresponding anodic/cathodic peak current. Luminescence spectra of ITO glass, ITO quartz substrates, and [BMIM][PF₆] ($\lambda_{\text{ex}} = 330 \text{ nm}$). Schematics showing possible luminescence change by reversible control of electrochemical switching from Eu³⁺ to Eu²⁺ upon reduction and vice versa upon oxidation.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Table of Contents

