Supplementary Information

Electrochemically controllable emission and coloration by using Europium (III) complex and viologen derivatives

Kazuki Nakamura, Kenji Kanazawa and Norihisa Kobayashi

Experimental details

Materials

Europium acetate tetrahydrate and hexafluoro acetylacetonato (hfa) were purchased from Tokyo Kasei Industries Ltd. 1,1'-Diheptyl-4,4'-bipyridinium Dibromide (HV^{2+}) was purchased from Aldrich co. Ltd. Propylene carbonate (Wako Pure Chemical Industries, Ltd.) was used as a solvent after removing water by molecular sieves. Tetra-n-butylammonium perchlorate (TBAP) (Wako Pure Chemical Industries, Ltd.) was used as an electrolyte (50 mmol/L) without further purification.

Synthesis of Tris(hexafluoroacetylacetonato)europium ($Eu(hfa)_3(H_2O)_2$)

Europium acetate monohydrate (5.0 g, 12.5 mmol) was dissolved in 50 mL of distilled water by stirring at 0 ±C. A solution of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 g, 33.6 mmol) was added dropwise to the above solution. The mixture produced a precipitation of white yellow powder after stirring for 3 h. The reaction mixture was filtered. The resulting white yellow needle crystals were recrystallized in methanol/water. Yield: 85%. Anal. Calcd for $C_{15}H_7O_8F_{18}Eu$: C, 22.48; H, 0.88%. Found: C, 22.12; H, 1.05%.

Photophysical measurements

UV-vis absorption spectra of the samples were measured using a spectrophotometer (JASCO, V-570) by using quartz cells (path length: 1.0 cm). Photoluminescence spectra were obtained using a spectrofluorometer (JASCO, FP-6600). Excitation wavelength of the samples was 337 nm. The emission lifetimes were determined by using a N_2 laser with a 337-nm wavelength and 4-ns pulse width (Spectra-Physics, VSL337) and a photomultiplier (Hamamatsu Photonics, H10721-20MOD, response time 0.8 ns). Samples were excited by nanosecond pulse of N_2 laser (337 nm). Emission from the sample was guided to the photomultiplier through a sharp-cut filter. Emission decays were monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to single-pulse excitation. The quantum yields were determined by standard procedures with an integral sphere (JASCO, ILF-533, diameter 10 cm) mounted on a spectrofluorometer (JASCO, FP-6600). The solution for optical measurements was purged with nitrogen gas for 20 min before each measurement.

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 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). The solution for electrochemical studies was purged with nitrogen gas for 20 min before each experiment. In order to measure the emission spectra and the emission lifetime under voltage application, the DC voltage was applied to the cell by using DC source (HIOKI 7011 DC signal source).

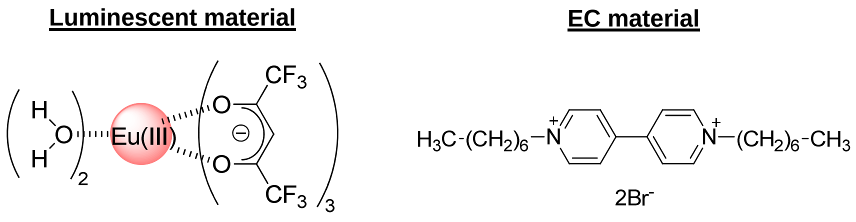
Preparation of the cells

A two electrodes cell was constructed with ITO glass electrodes and plastic spacer (70 μm; Lintec Co.). The PC solution containing $Eu(hfa)_3(H_2O)_2$, HV^{2+}, and TBAP was sandwiched between ITO electrodes to evaluate the electrochromic and emission property. Concentration of the $Eu(hfa)_3(H_2O)_2$, HV^{2+} and TBAP were 10 mmol/L, 10 mmol/L and 200 mmol/L, respectively.

The dual mode representations of numerical characters were carried out by using 7-segments patterned ITO electrodes. The DMD cell was fabricated by sandwiching PC solution of $Eu(hfa)_3(H_2O)_2/HV^{2+}$ and TBAP between 7-segments patterned ITO electrode and plane ITO electrode with keeping inter-electrodes distance of 70 μm by plastic spacer (Fig. S5). The concentration of $Eu(hfa)_3(H_2O)_2$, HV^{2+} and TBAP were were 10 mmol/L, 10 mmol/L and 200 mmol/L, respectively. The negative voltage was applied to certain patterned segments by using DC source (HIOKI 7011 DC signal source).

Fig. S1

Chemical structures of luminescent material and electrochromic material.



$Eu(hfa)_3(H_2O)_2$ HV^{2+}

Fig. S2

Emission spectra of $Eu(hfa)_3(H_2O)_2$ with HV^{2+} (Solid line) and $Eu(hfa)_3(H_2O)_2$ without HV^{2+} (dashed line). Concentration of the $Eu(hfa)_3(H_2O)_2$ and HV^{2+} were 1 mmol/L, excitation wavelength was 337 nm.

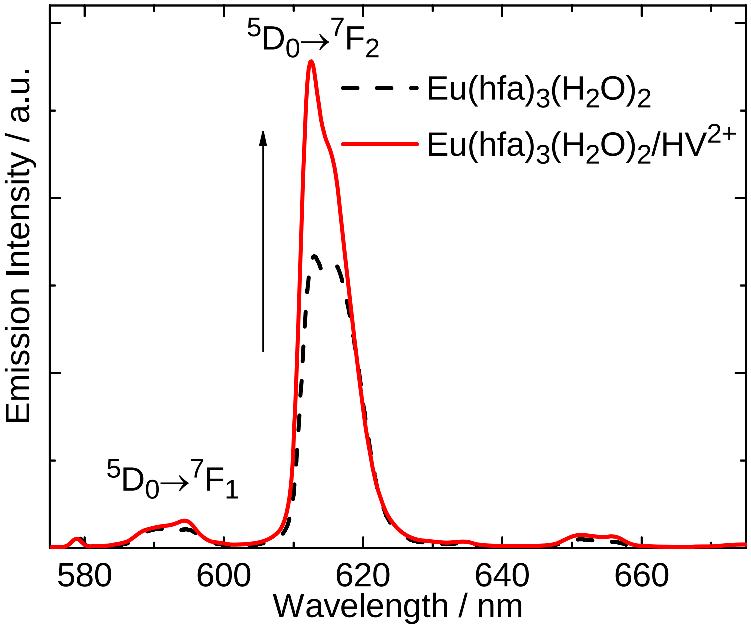


Fig. S3

Emission spectra of $Eu(hfa)_3(H_2O)_2$ in the two electrodes cell (Solid line: open circuit condition, dashed line: under bias voltage of 2.2 V). Concentration of the $Eu(hfa)_3(H_2O)_2$ HV^{2+} and TBAP were 10 mmol/L, 10 mmol/L and 200 mmol/L, respectively. Excitation wavelength was 337 nm.

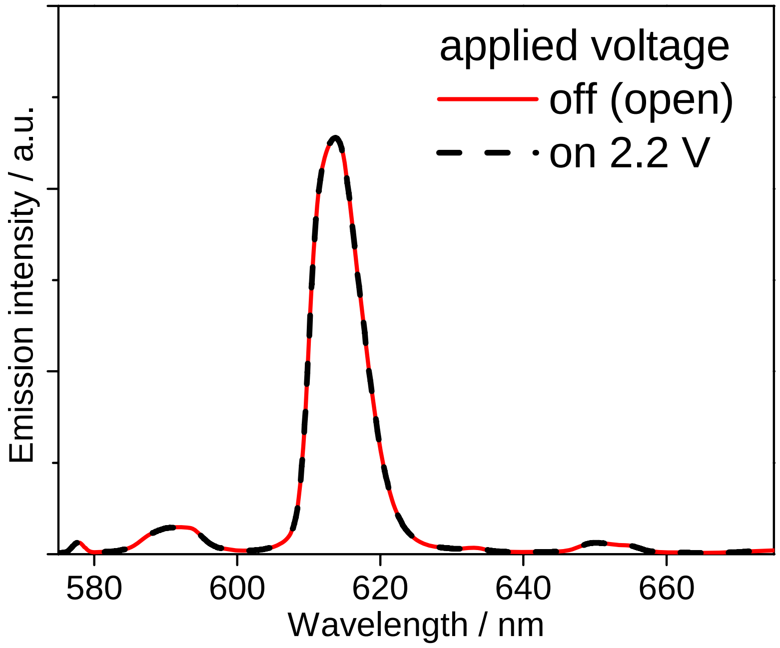


Fig. S4

Emission decay profiles of the two electrodes cell before voltage application (0 s), 3 s after voltage application and 50 s after voltage application. The profiles were shown on logarithmic scale. Excitation laser was nanosecond N_2 laser (337 nm).

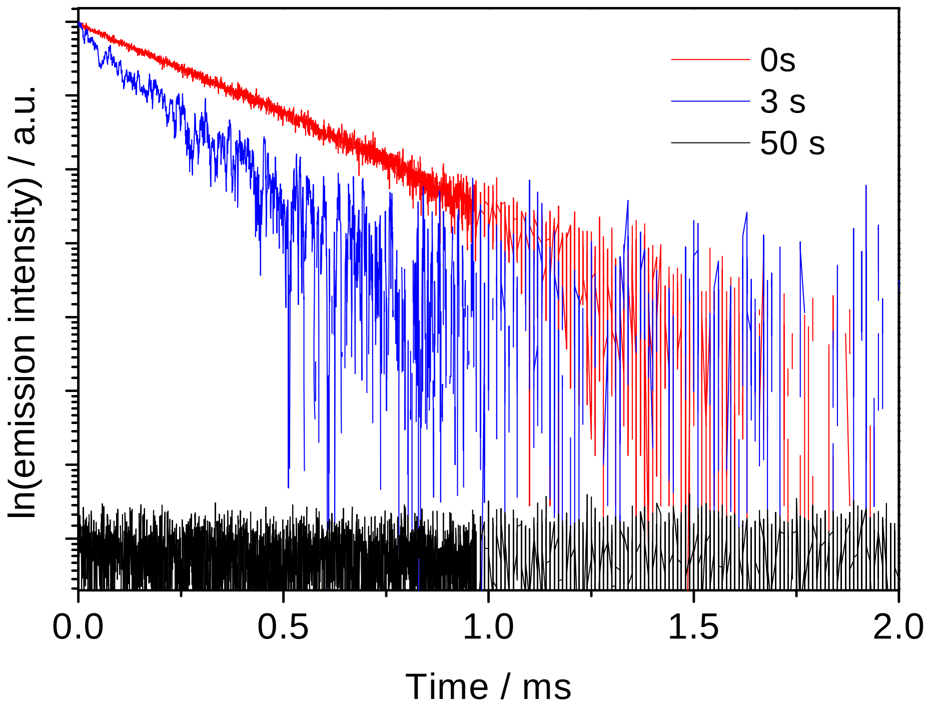


Fig. S5

Schematic illustrations of the 7-segments patterned electrode and device configuration for demonstration of the dual mode representation.