### Supporting information

# Red luminescence control of Eu(III) complex by utilizing the multi-colored electrochromism of viologen derivatives

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#### **Table of Contents**

1.	Characterization of 1,1'-diheptyl-4,4'-vinylenebipyridinium dibromide (HVP <sup>2+</sup> )S1		
2.	Absorption spectra of viologen derivatives/Eu(hfac) <sub>3</sub> (TPPO) <sub>2</sub> solution		
	with and without potential application		
3.	Emission spectra of Eu(hfac) <sub>3</sub> (TPPO) <sub>2</sub> solution		
4.	Absorption spectra of $Eu(hfac)_3(H_2O)_2$ , $HV^{2+}$ , $HVP^{2+}$ , and $DNP^{2+}$ S5		
5.	Absorption spectrum of $Eu(hfac)_3(H_2O)_2$ and excitation and emission spectra		
	of Gd(hfac) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> S6		
6.	Estimations of coloration efficiencies of EC molecules		



# 1. Characterization of 1,1'-diheptyl-4,4'-vinylenebipyridinium dibromide

(HVP<sup>2+</sup>)

**Fig. S1**<sup>1</sup>H NMR spectrum of  $HVP^{2+}$  in dmso- $d_6$ .



Fig. S2 FT-IR spectrum of  $HVP^{2+}$ .

2. Absorption spectra of each viologen derivatives/Eu(hfac)<sub>3</sub>(TPPO)<sub>2</sub> solution with and without potential application



**Fig. S3** Absorption spectra of  $Eu(hfac)_3(TPPO)_2/HV^{2+}$  in a 200 mmol/L TBAP/DMSO electrolyte solution with a three-electrode cell by application potential at -0.52 V (vs. Ag/AgCl) for 6 s. Insets are coloration changes of samples. Concentrations of  $Eu(hfac)_3(TPPO)_2$  and  $HV^{2+}$  are 5 mmol/L.



**Fig. S4** Absorption spectra of  $Eu(hfac)_3(TPPO)_2/HVP^{2+}$  in a 200 mmol/L TBAP/DMSO electrolyte solution with a three-electrode cell by application potential at -0.55 V (vs. Ag/AgCl) for 6 s. Insets are coloration change of samples. Concentrations of  $Eu(hfac)_3(TPPO)_2$  and  $HVP^{2+}$  are 5 mmol/L.



Fig. S5 Absorption spectra of  $Eu(hfac)_3(TPPO)_2/DNP^{2+}$  in a 200 mmol/L TBAP/DMSO electrolyte solution with a three-electrode cell by application potential at -0.15 V (vs. Ag/AgCl) for 6 s. Insets are coloration change of samples. Concentrations of  $Eu(hfac)_3(TPPO)_2$  and  $DNP^{2+}$  are 5 mmol/L.

#### 3. Emission spectra of Eu(hfac)<sub>3</sub>(TPPO)<sub>2</sub>



Fig. S6 Emission spectra of  $Eu(hfac)_3(TPPO)_2$  solution without viologen derivatives-based on the two electrodes cell by irradiated at 337 nm [solid line: open-circuit condition, dashed line: under the application of -2.1 V (s)].

# 4. Absorption spectra of HV<sup>2+</sup>, HVP<sup>2+</sup>, and DNP<sup>2+</sup>



**Fig. S7** Normalized absorption spectra of  $HV^{2+}$  (blue solid line),  $HVP^{2+}$  (magenta solid line), and  $DNP^{2+}$  (green solid line). As the solvents for estimation of bandgaps, propylene carbonate for  $HV^{2+}$  and dmso for  $HVP^{2+}$  and  $DNP^{2+}$  were used.

# 5. Absorption spectrum of $Eu(hfac)_3(TPPO)_2$ and excitation and emission spectra of $Gd(hfac)_3(H_2O)_2$



Fig. S8 Normalized absorption spectrum of 10 µM Eu(hfac)<sub>3</sub>(TPPO)<sub>2</sub> in DMSO.



Fig. S9 Normalized excitation and emission spectra of 10  $\mu$ M Gd(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in mixture solvents of ether, ethanol, and toluene (volume ratio = 2:1:1) at 77 K.

#### 6. Estimations of coloration efficiencies of EC molecules

Coloration efficiency  $(\eta)$  is an important characteristic of EC molecules. It is defined as the change in the optical density ( $\Delta O.D.$  or  $\Delta A$ ) for the charge consumed ( $\Delta Q$ ) per unit electrode (area, S) during the switching of the solution from dication to monocation radical species of EC molecules. The corresponding equation is given below:

$$\eta (cm^2/C) = \frac{\Delta A}{\Delta Q (C) / S (cm^2)}$$

where  $\Delta A$  and S are absorbance difference between dication and monocation radical state of EC molecules and reaction area of electrode (1.74 cm<sup>2</sup> in this report). From this equation and the slopes of approximate straight lines for  $\Delta A$  versus charge density plot as given in inset of Fig. S4,  $\eta$  of EC molecules were estimated as seen in Table S1. The values of HV<sup>++</sup>, HVP<sup>++</sup>, and DNP<sup>++</sup> were almost coincided with previous reports.

Further, molar extinction coefficient ( $\varepsilon$ ) is determined by Lambert-Beer law as given below:

$$\varepsilon = \frac{\Delta A}{C \times L} = \frac{\Delta A}{Q / (F \times V) \times L} = \frac{\Delta A}{Q} \times F \times V \times L$$

where C, L, F, and V are molar concentration of EC molecule, optical length, Faraday constant, and solution volume. In this paper, L, F, and V were 1.0 cm,  $9.65 \times 10^4$  C/mol, and  $1.57 \times 10^{-3}$  L, respectively. From this equation and the slopes of approximate straight line for  $\Delta A$  versus charge density plot as given in inset of Fig. S10,  $\varepsilon$  of EC molecules in monocation radical state were estimated as seen in Table S1.



**Fig. S10** Plots of absorbance difference ( $\Delta A$ ) versus charge density of a monochromatic wavelength at (a) 604 nm (HV<sup>+.</sup>), (b) 519 nm (HVP<sup>+.</sup>), and (c) 867 nm (DNP<sup>+.</sup>).

Compound	$\lambda_{abs}$	η	З
	[nm]	$[cm^2/C]$	$[M^{-1}cm^{-1}]$
$\mathrm{HV}^{2+}$	604	133	13000
HVP <sup>2+</sup>	519	468	45100
DNP <sup>2+</sup>	867	137	13200

 Table S1 Coloration efficiencies and molar extinction coefficients of monocation

radical states of EC molecules.



Fig. S11 Coloration efficiencies of monocation radical species of viologen derivatives.