

Supporting information

Electrochemical luminescence modulation in a Eu(III) complex-modified TiO₂ electrode

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1. SEM-EDS analysis of $\text{Eu}(\text{tta})_3\text{dcbpy}$ -modified electrode

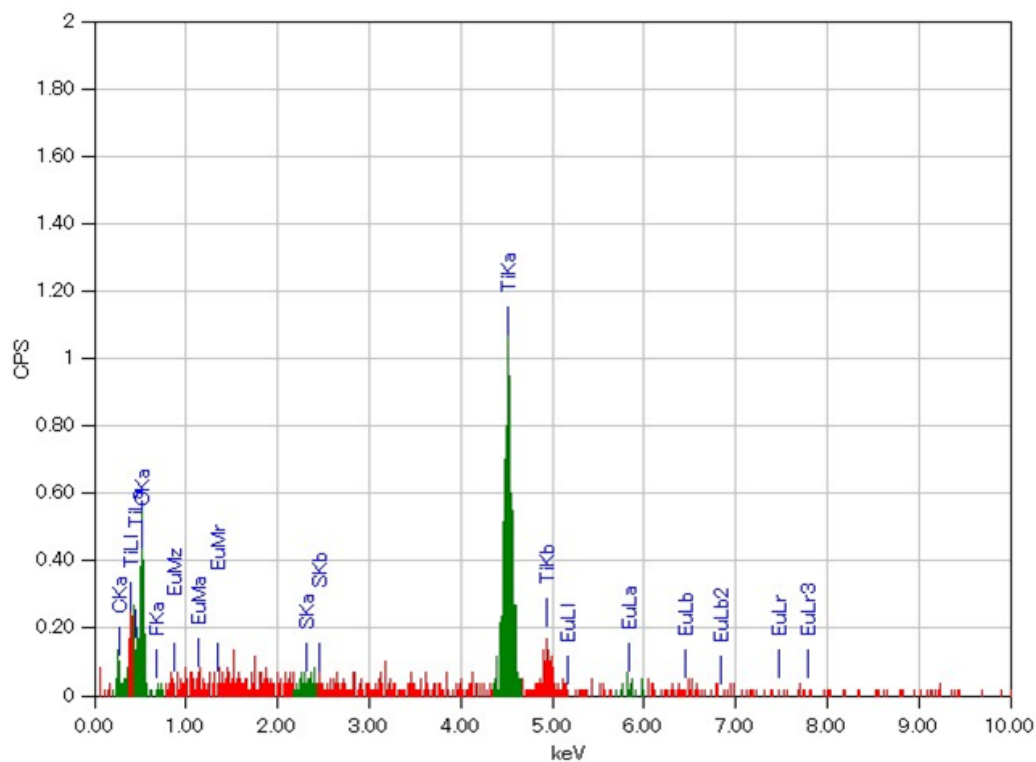


Fig. S1 EDS spectrum of the $\text{Eu}(\text{tta})_3\text{dcbpy}$ -modified electrode.

Table. S1 Elemental ratio of the $\text{Eu}(\text{tta})_3\text{dcbpy}$ -modified electrode.

Element	Atomic [%]
C	13.85
O	61.30
F	—
S	0.14
Ti	23.97
Eu	0.73

2. Measurement configuration of the fluorescence spectroelectrochemical cell

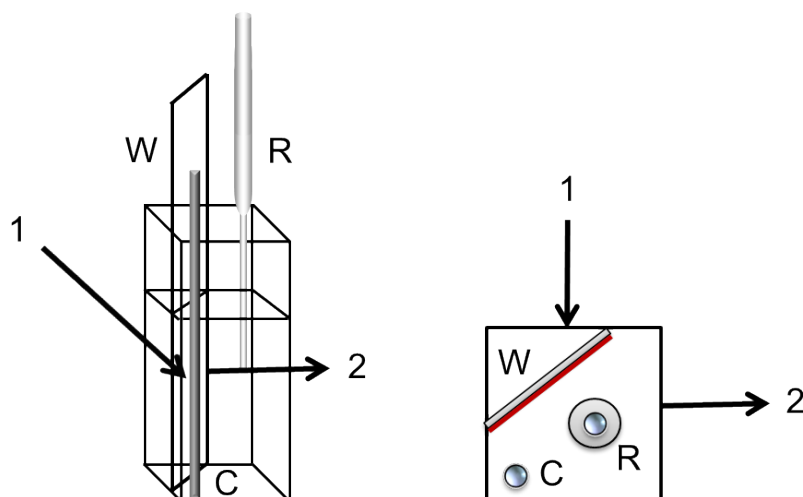


Fig. S2 Schematic representation of measurement configuration of the fluorescence spectroelectrochemical cell: connection for (W) working, (R) reference, and (C) counter electrode: Eu(tta)₃dc bpy-modified electrode, Ag/AgCl, and Pt wire. (1) Excitation source. (2) Emission detector.

3. Emission decay profiles of $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ and $\text{Eu}(\text{tta})_3\text{dcbpy}$ -modified TiO_2 electrode

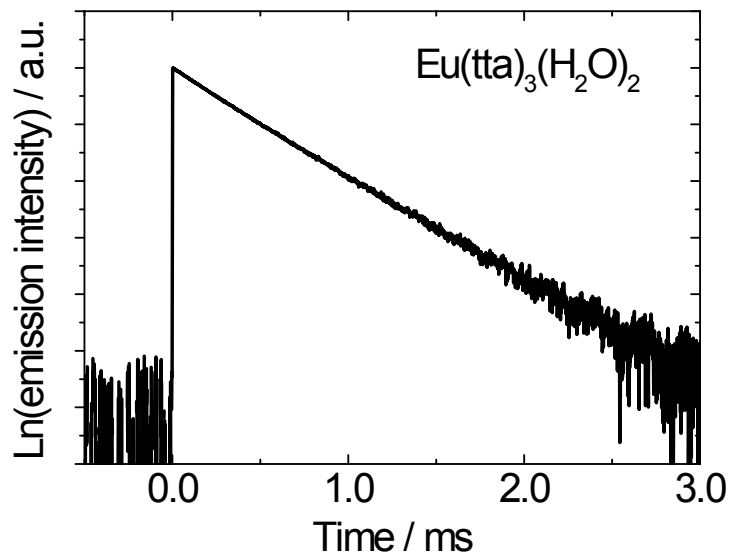


Fig. S3 Emission decay profile of the PC solution containing $50 \mu\text{M}$ $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ by using the quartz cell whose path length is 1 mm. Excitation wavelength is 337 nm.

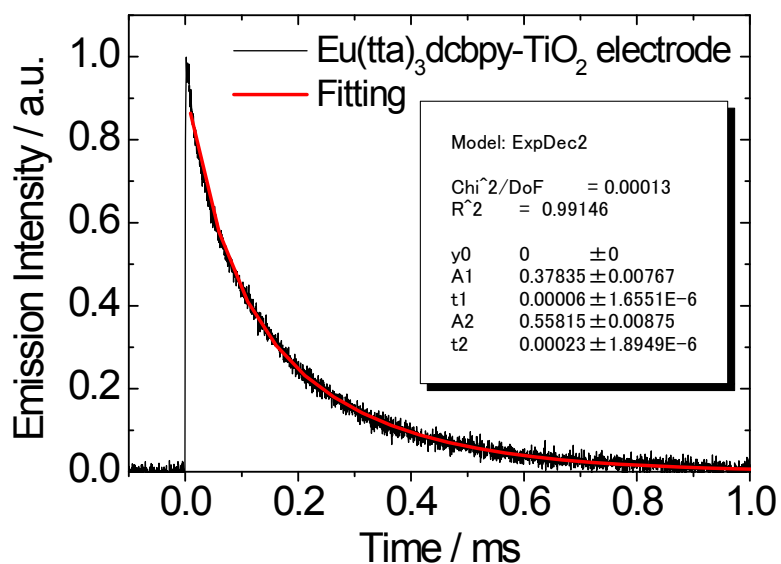


Fig. S4 Emission decay curves of $\text{Eu}(\text{tta})_3\text{dcbpy}$ -modified TiO_2 electrode without solution. Excitation wavelength is 337 nm. Fitting function was employed biexponential decay.

4. Measurement configuration of the fluorescence spectroelectrochemical cell

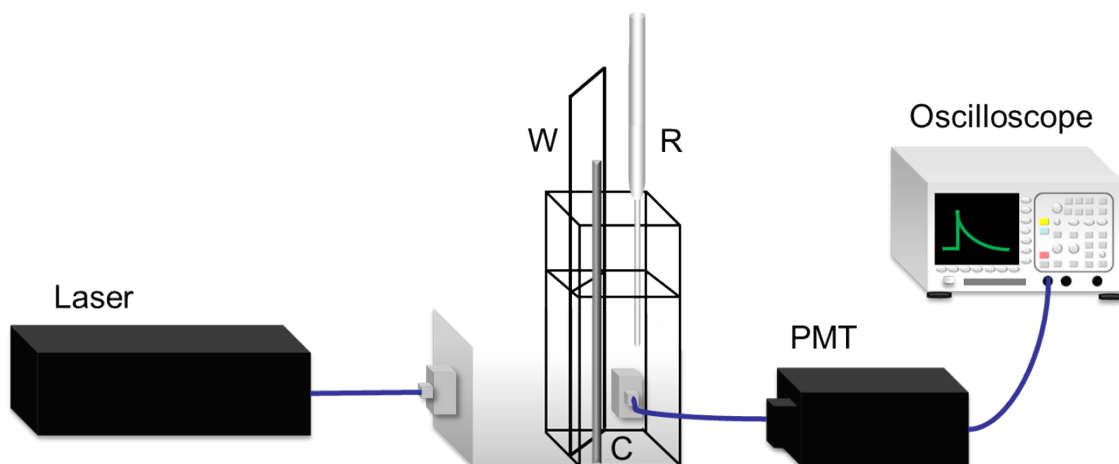


Fig. S5 Schematic representation of emission lifetime measurement system: connection for (W) working, (R) reference, and (C) counter electrode: $\text{Eu}(\text{tta})_3\text{dcbpy}$ complex-modified electrode, Ag/AgCl , and Pt wire. Wavelength of the laser is 337 nm.

5. Emission decay profiles of $\text{Eu}(\text{tta})_3\text{dcbpy}$ modified TiO_2 electrode

under open circuit and application potential

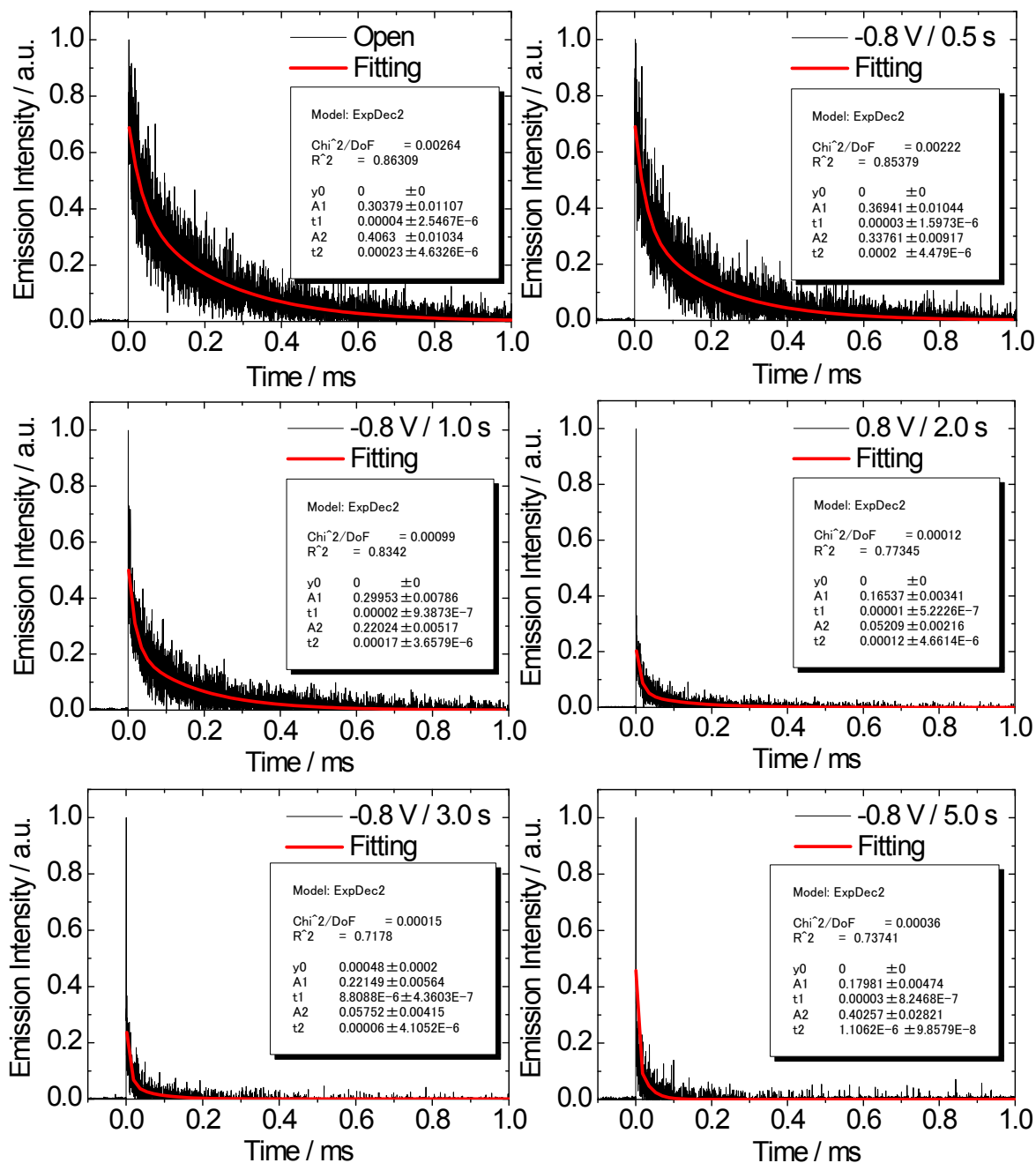


Fig. S6 Emission decay curves of $\text{Eu}(\text{tta})_3\text{dcbpy}$ modified on TiO_2 electrode by irradiated at 337 nm when the potential at -0.8 V (vs. Ag/AgCl) was applied to the cell for 0, 0.5, 1, 2, 3, and 5 s.

6. Absorption spectra of tta and $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$

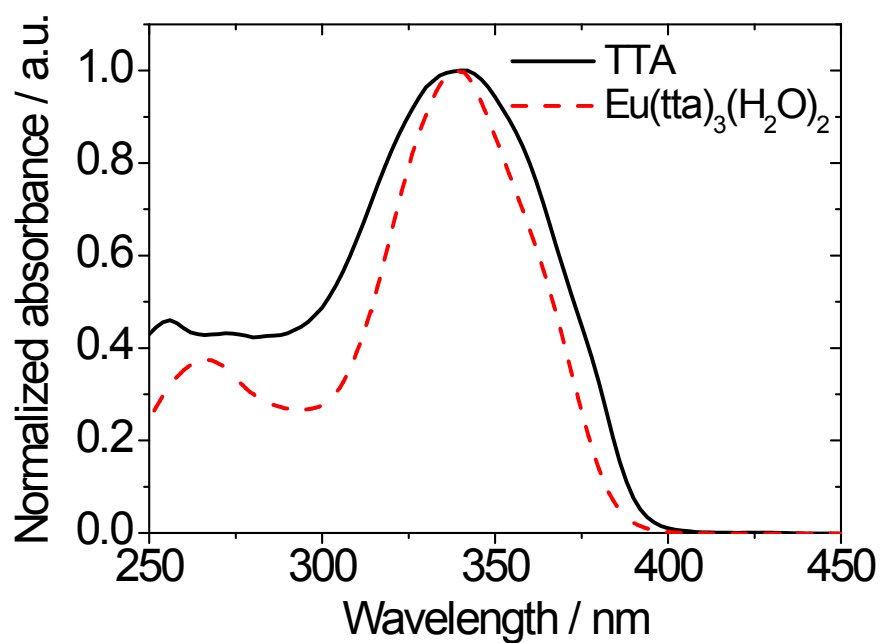


Fig. S7 Normalized absorption spectra of TTA (10 μM , black line) and $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ (10 μM , red dashed line) in PC solution.

7. Cyclic voltammograms of TTA and $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$

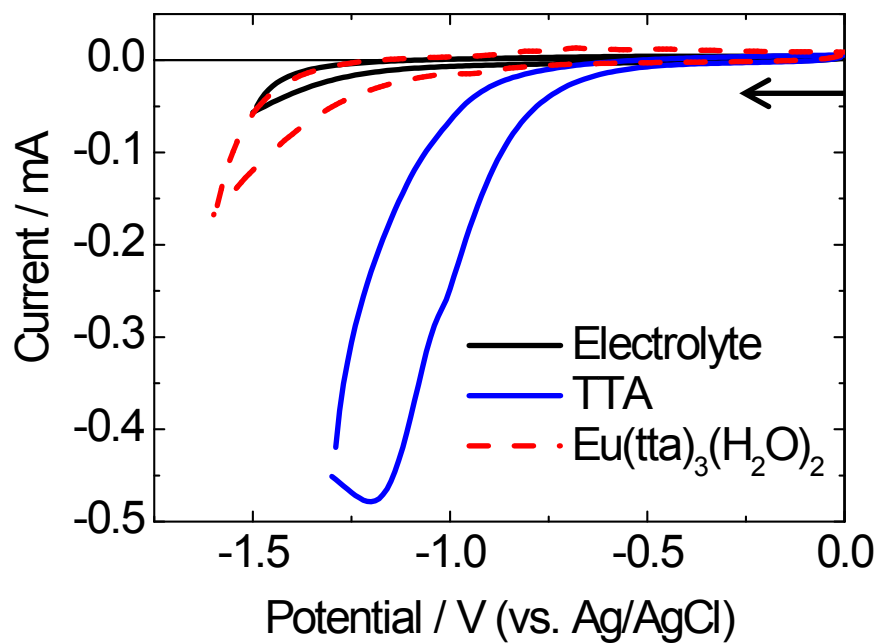


Fig. S8 CVs of PC solution containing in tta (10 mM, blue line) or $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ (10 mM, red dashed line) and LiClO_4 (200 mM, black line). Scan rate was 50 mV/s.