

Electronic Supplementary Information (ESI)

**Electrochemically Triggered Upconverted Luminescence for  
Light-Emitting Devices**

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**Contents**

1. Experimental

1-1. Reagents -----	S2
1-2. Fabrication of the ECL device -----	S2
1-3. Electrochemical Measurements -----	S2
1-4. Measurements of ECL properties -----	S3
1-5. Measurements of optical properties -----	S3

2. TTET and TTA-UC between Ru(bpy) <sub>3</sub> <sup>2+</sup> and DPA in electrolyte via photo-excitation -----	S4
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3. Spectroelectrochemistry measurement-----	S6
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## 1. Experimental

### 1-1. Reagents

All the chemicals were commercially available and used as received. Tris(2,2'-bipyridine)ruthenium(II) Bis(hexafluorophosphate) was purchased from Tokyo Chemical Industry Co. Ltd., Japan, and used as an orange electrochemiluminescent material. 9,10-diphenylanthracene was purchased from Tokyo Chemical Industry Co. Ltd., Japan, and used as a blue electrochemiluminescent material. Tetra-n-butyl ammonium perchlorate (TBAP) was purchased from Kanto Chemical Co. Japan and used as the supporting electrolyte. Propylene carbonate (PC) was purchased from Tokyo Chemical Industry Co. Ltd., Japan, and used as the solvent for the ECL electrolyte solution. Toluene was purchased from Sigma-Aldrich Co., USA, and used as the solvent for the ECL electrolyte solution. In order to prepare the ECL electrolyte solution, Ru(bpy)<sub>3</sub><sup>2+</sup> and DPA were used at various concentrations with 100 mmol L<sup>-1</sup> TBAP dissolved in PC/toluene (volume ratio = 1:1).

### 1-2. Fabrication of the ECL device

Indium-tin oxide (ITO) electrodes were purchased from Sanyo Vacuum Industries Co. Ltd. Silicone spacers were purchased from Mitsubishi Chemical Corporation. The ECL devices were fabricated by sandwiching ECL solutions between pairs of ITO electrodes, with inter-electrode distances kept at 300 μm by silicone spacers. Cells were simply sealed with clips. The effective electrode area of the ECL devices was 1.0 × 1.0 cm<sup>2</sup>. The ECL devices were fabricated in a glove box filled with Ar atmosphere.

### 1-3. Electrochemical Measurements

Cyclic voltammograms (CVs) were acquired using an ALS440 A (CH Instruments, Inc., USA) equipped with a computer. For the analysis of redox properties of ECL materials, a three-electrode cell was fabricated with indium tin oxide (ITO) as the working electrode, a Pt disk ( $\varphi = 3$  mm) as the counter electrode, and an Ag/Ag<sup>+</sup> electrode as the reference electrode. The reference electrode was prepared by injecting Ag<sup>+</sup> solution (10 mM AgNO<sub>3</sub>, 100 mM TBAP in PC) into a sample holder with ion-permeable glass (purchased from BAS Co., Ltd, Japan) and sealing with a cap having Ag wire ( $\varphi = 1$  mm).

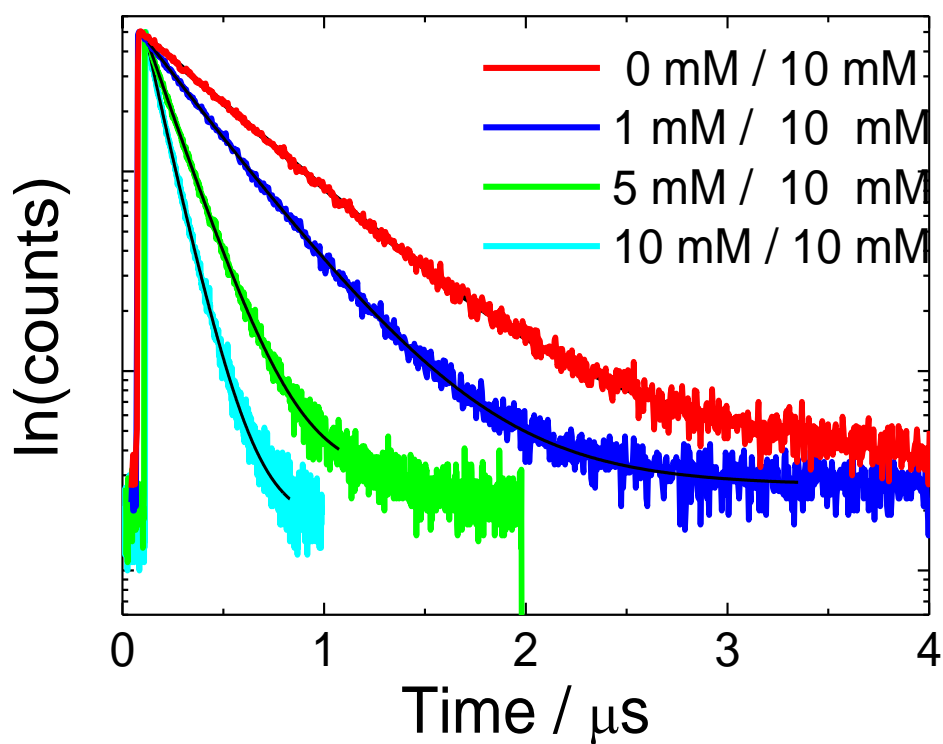
#### **1-4. Measurements of ECL properties**

AC voltages were applied to the ECL devices using a function generator (SG-4115, Iwatsu Electric Co., Ltd, Japan) and an electrical amplifier (NF 4010, NF Techno Commerce Co., Ltd, Japan). ECL spectra were measured using a photonic multichannel analyzer (PMA C10027, Hamamatsu Photonics, Japan). All experiments were conducted in a glove box filled with Ar atmosphere.

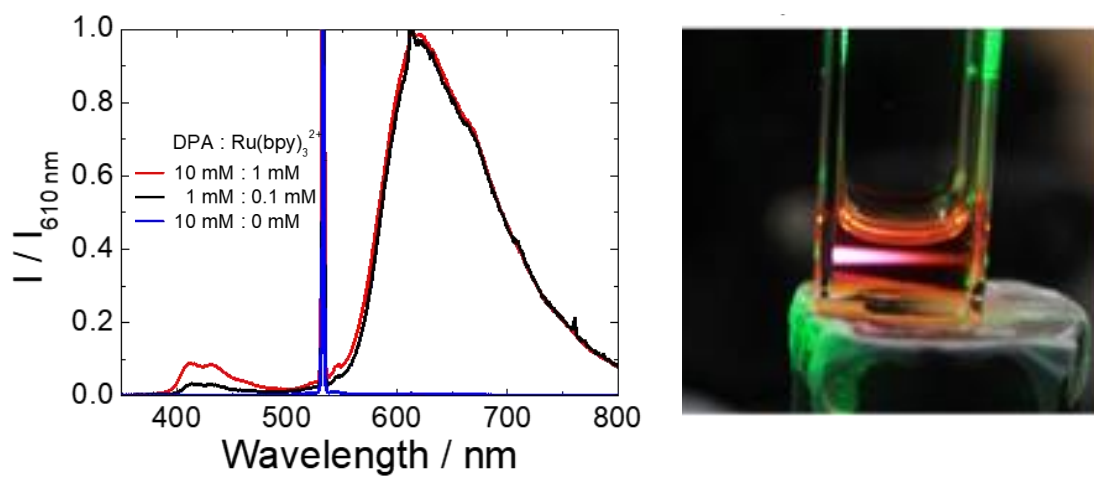
#### **1-5. Measurements of optical properties**

Nitrogen-gas bubbling was conducted to remove oxygen from solutions before optical measurement. Photoluminescence spectra of Ru(bpy)<sub>3</sub><sup>2+</sup>/DPA solutions were obtained at an excitation wavelength of 532 nm (Nd: YAG, 2 $\omega$ , 10 mW) using a photonic multichannel analyzer (PMA C10027, Hamamatsu Photonics, Japan). The emission lifetimes were determined by using a time-resolved fluorescence spectrometer (IBH 5000U-CS, HORIBA Jobin Yvon IBH Ltd., UK). Observed time resolved emission decays were fitted by using single exponential function. These measurements were conducted under ambient conditions (temperature: 25 C; humidity: 50–60%; oxygen concentration: 20%).

2. TTET and TTA-UC between  $\text{Ru}(\text{bpy})_3^{2+}$  and DPA in electrolyte via photo-excitation

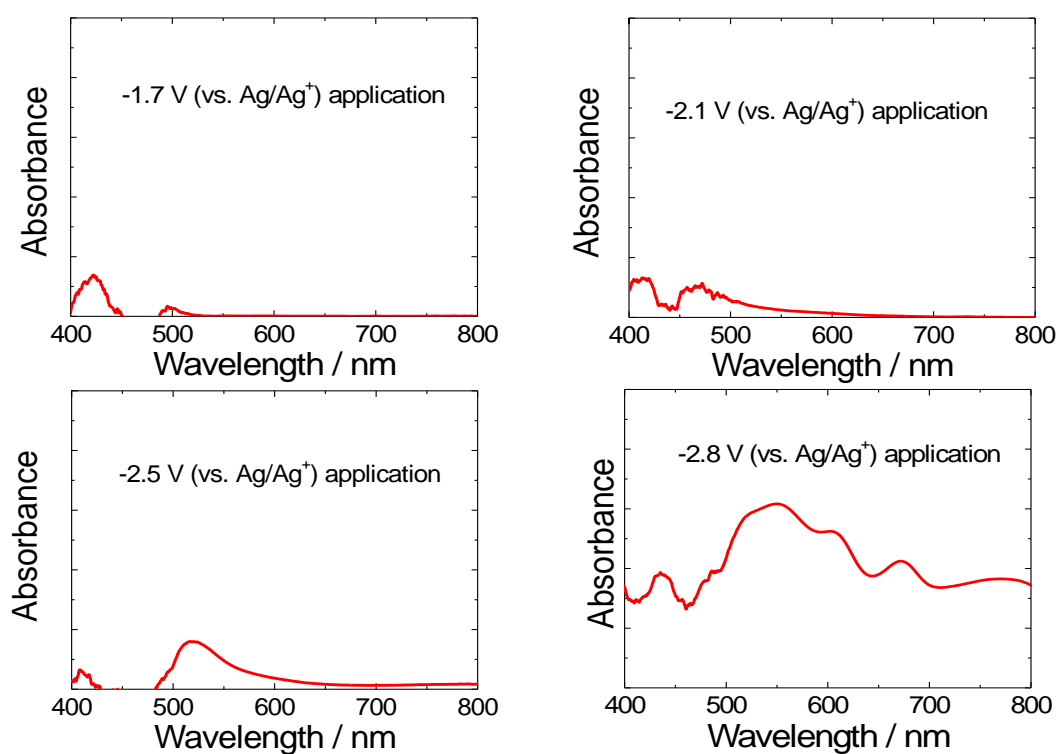


**Figure S1.** Emission decay of  $\text{Ru}(\text{bpy})_3^{2+}$  in PC/toluene solution containing  $\text{Ru}(\text{bpy})_3^{2+}$  (10 mM) and DPA (0–10 mM).



**Figure S2.** Photoluminescence spectra of DPA (blue) and  $\text{Ru}(\text{bpy})_3^{2+}$ /DPA in PC/toluene. Excitation wavelength was 532 nm.

### 3. Spectroelectrochemistry measurement



**Figure S3.** Absorption spectra of the Ru(bpy)<sub>3</sub><sup>2+</sup>/DPA mixed solution when potentials of -1.7V, -2.1V, -2.5V and -2.8V (vs. Ag/Ag<sup>+</sup>) were applied in three-electrode cell.