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Performance improvement of yellow emitting electrochemiluminescence devices: Effects of frequency control and coreactant pathway



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ARTICLE INFO	A B S T R A C T		
Keywords: Electrochemiluminesence Luminophore Electrochemical devices Brightness enhancement	In this work, we propose an electrochemiluminescence (ECL) luminophore, 2,2'-bipyridylbis(2-phenylpyridine) iridium(III) hexafluorophosphate ($[Ir(ppy)_2(bpy)][PF_6]$) (1), emitting yellow-colored light for displaying a variety of ECL colors. The synthesized luminophore 1 is optically and electrochemically analyzed. The ECL electrolytes are very simply composed of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI] [TFSI]), sandwiched between two transparent electrodes used for the devices. The resulting ECL devices are characterized by a low-voltage operation and quick response independent of frequency. We also suggest an efficient method for improving the ECL brightness by incorporating 2,2'-bipyridylbis[2-(2',4'-difluorophenyl) pyridine]iridium(III) hexafluorophosphate ($[Ir(diFppy)_2(bpy)][PF_6]$) (2) as a coreactant. The intensity of the emitted yellow light is doubled, when 60 mol% of 2 is included in the mixed-luminophore system. Additionally, we further enhanced the luminance of yellow light emitting ECL devices by adjusting the frequency of applied AC voltage, leading to ~3.5 times higher brightness at 500 Hz.		

1. Introduction

Electrochemiluminescence (ECL) is light emission from excited luminophores generated through electrochemical redox reactions [1–6]. ECL devices have been widely studied in recent years, not only for sensing applications with remarkable sensitivity and selectivity [7,8] but also for electrochemical displays having high potential. Although conventional emissive displays such as organic light emitting diodes (OLEDs) have already been commercialized as a light source for electronics or electrical lighting [9,10], there are certain limitations to their structures and fabrication processes [11]. For instance, an energetically balanced multilayer configuration is essential for efficient electron injection and charge transport, and a vacuum process is usually required for deposition. In contrast, ECL devices have advantageous features such as a simple device structure (two electrodes and an ECL electrolyte) and an easy device fabrication through a solution process.

Nevertheless, there are still a few problems to be overcome for the practical display applications of ECL devices. One example is the narrow spectrum for the color of emitted light using ECL. Tris(2,2'-bipyridyl)-dichlororuthenium(II)- (Ru(bpy)_3^{2+}) , 2,2'-bipyridylbis[2-(2',4'-di-fluorophenyl)pyridine]iridium(III)-complexes (Ir(diFppy)_2(bpy)^+), and 9,10-diphenyl anthracene have been reported as representative ECL materials for red (R), green (G), and blue (B) components, respectively

[12–15]. In principle, the color range of an emitted light can be expanded by a combination of three primary RGB colors. However, a complex pixelization process and fine performance tuning of each component are necessary. These issues can be overcome by the development of new luminophores that directly emit colors other than RGB.

In this work, we present yellow-light emitting ECL luminophore, 2,2'-bipyridylbis(2-phenylpyridine)iridium(III) hexafluorophosphate ([Ir(ppy)₂(bpy)][PF₆]). The prepared luminophore was optically and electrochemically characterized using UV-vis spectrometry and cyclic voltammetry, respectively. To fabricate the devices, [Ir(ppy)₂(bpy)] [PF₆] was dissolved in 1-ethyl-3-methylimidazolium bis-(tri-fluoromethylsulfonyl)imide ([EMI][TFSI]) and sandwiched between two transparent electrodes. When we applied an AC voltage at 60 Hz, the devices emitted a yellowish light with a CIE color coordinate of (x,y) = (0.53, 0.45) via annihilation pathway, as shown in equations (1) through (4).

Ir(ppy) ₂ (bpy) ⁺	+ e ⁻	\rightarrow Ir(ppy) ₂ (bpy) ^{•0}	(1)
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 $Ir(ppy)_2(bpy)^+ - e^- \rightarrow Ir(ppy)_2(bpy)^{\cdot 2+}$ (2)

$$Ir(ppy)_{2}(bpy)^{*0} + Ir(ppy)_{2}(bpy)^{*2} \rightarrow Ir(ppy)_{2}(bpy)^{+*} + In(ppy)_{2}(bpy)^{+}$$
(3)

$$Ir(ppy)_2(bpy)^{+*} \to Ir(ppy)_2(bpy)^{+} + hv$$
(4)

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The device also exhibited a quick turn-on response whenever the AC voltage polarization was switched, similar to those of other ECL materials in ionic liquids or an ion gel [16,17]. This rapid response (~0.15 ms scale) was also shown irrespective of the frequency of applied AC voltages. Furthermore, we propose two efficient methodologies to enhance the brightness of yellow ECL by employing mixed luminophore systems consisting of [Ir(ppy)₂(bpy)][PF₆] and [Ir (diFppy)₂(bpy)][PF₆], and/or by modulating frequency. The included Ir (diFppy)₂(bpy)⁺ can serve as a coreactant, which leads to the additional formation of excited Ir(ppy)₂(bpy)^{+*} through the coreactant pathway. Additionally, we optimized the frequency of AC voltages applied to ECL devices with a mixed luminophore. As a result, the luminance of the yellow light was ~3.5 times increased in comparison with that of Ir(ppy)₂(bpy)⁺-only device operating at 60 Hz.

2. Experimental

2.1. Materials

All chemical reagents were purchased from Sigma-Aldrich except for iridium(III) chloride hydrate (IrCl₃·xH₂O) (Tokyo Chemical Industry Co. Ltd.), and used without further purification. The 2,2'-bipyridylbis (2-phenylpyridine)iridium(III) hexafluorophosphate ([Ir(ppy)₂(bpy)] [PF₆]) (1) and 2,2'-bipyridylbis[2-(2',4'-difluorophenyl)pyridine]iridium(III) hexafluorophosphate ([Ir(diFppy)₂(bpy)][PF₆]) (**2**) were synthesized as follows [18,19]. As an example, the synthetic route of 1 is given in Fig. 1a. In brief, a mixture of IrCl₃·xH₂O (1.67 mmol, 1 eq) and 2-phenylpyridine (3.68 mmol, 2.2 eq) dissolved in 2-ethoxyethanol and DI-water (4:1, v/v) was refluxed under a nitrogen atmosphere for 24 h. The yellowish solution was then cooled to room temperature. The precipitates, dicholorotetrakis[2-(2-pyridinyl)phenyl]diiridium(III) ([Ir (ppy)₄][Cl]₂), were filtered and dried in vacuum for 24 h. The intermediate (4.66 mmol, 1eq) was dissolved in ethylene glycol (30 mL), followed by the addition of 2,2'-bypyrindyl (1.03 mmol, 2.2eq) to the solution. After refluxing for 20 h, the reddish solution was cooled to room temperature. Then, an aqueous solution containing excess ammonium hexafluorophosphate (NH₄PF₆) was subsequently injected dropwise for an anion exchange reaction. The precipitated product 1 was filtered, collected, and dried in vacuum for 24 h ¹H NMR (400 MHz,

CD₃COCD₃, δ): 8.85 (d, 2H), 8.30 (t, 2H), 8.24 (d, 2H), 8.10 (d, 2H), 7.96 (t, 2H), 7.89 (d, 2H), 7.83 (d, 2H), 7.71 (t, 2H), 7.15 (t, 2H), 7.03 (t, 2H), 6.92 (t, 2H), 6.36 (d, 2H) [20]. An ionic liquid, 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([EMI][TFSI]), was synthesized via an anion exchange reaction between 1-ethyl-3-methylimidazolium bromide ([EMI][Br]) and excess lithium bis-(trifluoromethylsulfonyl)imide (LiTFSI) in DI-water. The detailed preparation process is described elsewhere [21]. Patterned ITO-coated glasses (sheet resistance: $10 \Omega/sq$, Asahi Glass Co.) were cleaned with acetone (5 min), methanol (5 min), and isopropanol (5 min) under sonication, and were treated under UV/ozone prior to use.

2.2. ECL device fabrication

ECL devices with configurations of patterned ITO/ECL electrolyte/ patterned ITO were fabricated as follows. First, **1** (~3 wt% relative to [EMI][TFSI]) was completely dissolved in [EMI][TFSI] at 60 °C, and the solution was cast onto a glass substrate including two ITO line patterns. Double-sided tapes (thickness of ~88 µm) serving as both an adhesive and a spacer were placed around the cast ECL electrolyte, and another patterned ITO electrode was placed on top of them. It should be noted that the ITO lines at the top electrode were crossed vertically with those at the bottom electrode. Consequently, four square-shaped active areas (size of 2 mm × 2 mm each) were produced.

2.3. Device characterization

The ¹H NMR spectrum was recorded on a Bruker digital Avance III 400 using acetone- d_6 as a solvent. AC square waves at 60 Hz were applied using a function/arbitrary waveform generator (33210A, Keysight). The UV-vis absorption spectrum of the [EMI][TFSI] solution containing **1** was measured using a UV-vis spectrometer (V-730, Jasco) from 190 to 1100 nm at a scan rate of 400 nm/min. The cyclic voltammogram (CV) for **1** in acetonitrile (ACN) containing 100 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) (supporting electrolyte) was obtained using a potentiostat (Wave Driver 10, Pine Instrument) with a scan rate of 100 mV/s under an Ar atmosphere. Platinum disks were used for the working and counter electrodes, and a silver (Ag) wire was employed as a pseudo-reference electrode with an



Fig. 1. (a) Synthetic route and (b) ¹H NMR spectrum of 1 as an active electrochemiluminescent (ECL) luminophore used in this study.

internal standard, i.e. ferrocene (Fc). The emission spectra, ECL intensity, and CIE color coordinate were acquired using a spectroradiometer (CS-2000, Konica Minolta). Transient ECL profiles were recorded on an oscilloscope (TDS2024C, Tektronix) using a photodetector (PDA36A, Thorlabs).

3. Results and discussion

In comparison to typical organic solvents, [EMI][TFSI], a widely used ionic liquid, shows better thermal and electrochemical stability, and higher ionic conductivity without the need for additional salts [22,23]. Thus, [EMI][TFSI] and [EMI][TFSI]-based gel electrolytes have been employed in various electrochemical applications [24–26]. To function as AC-driven ECL materials, the production of stable oxidized/reduced luminophores that can react together is essential for the formation of an excited species. In addition, luminophores should be fully soluble in electrolytes such as [EMI][TFSI]. However, there are few ECL luminophore candidates satisfying these criteria. One representative is 2 emitting green-colored light through an annihilation route [27]. To decrease the band gap and derive the red-shifted color, we eliminated fluorine atoms on the phenylpyridine units (see Fig. 1a). In general, fluoro-substituents withdraw the electron density from the metal center, resulting in a stabilization of the d-orbitals of the metals and a higher oxidation potential [28,29]. Therefore, the selection of non-functionalized phenylpyridines is a valid approach to a decrease in the band gap. The successful preparation of the target 1 was confirmed by ¹H NMR spectroscopy. All peaks and integration values are wellmatched with the theoretical calculations (Fig. 1b).

Optical and electrochemical properties of **1** were investigated. Fig. 2a displays the absorption spectrum of **1** in [EMI][TFSI], which exhibited several noticeable peaks between 250 and 600 nm. For example, the peaks at ~310, ~376, ~408, and ~466 nm correspond to the singlet-intra-ligand- (¹ILCT), ligand-to-ligand- (¹LLCT), metal-to-ligand- (¹MLCT), and triplet metal-to-ligand charge-transfer (³MLCT) states, respectively [30]. We estimated the optical band gap ($E_{g,opt}$) using equation (5) [31].

$$E_{g,opt} = \frac{hc}{\lambda_{onset}}$$
(5)

where *h* is Plank's constant, and *c* is the speed of light. When considering the onset ($\lambda_{onset} \sim 501$ nm) of the absorption spectrum (see inset of Fig. 2a), E_{g,opt} of ~2.48 eV was extracted. To understand the electrochemical redox behaviors of **1**, a cyclic voltammogram (CV) was recorded, in which a ferrocene/ferrocenium (Fc/Fc⁺) couple was used as an internal standard. Fig. 2b clearly exhibits two redox peaks at +0.92 and -1.77 V, which correspond to the oxidation [Ir (ppy)₂(bpy)⁺ to Ir(ppy)₂(bpy)²⁺] and reduction [Ir(ppy)₂(bpy)⁺ to Ir (ppy)₂(bpy)⁻⁰] reactions, respectively. We also estimated the electrochemical band gap energy (E_{g,ec}) of **1** based on the onset potentials (E_{onset,ox} ~ +0.84 V, E_{onset,red} ~ -1.69 V) [32,33]. As a result, E_{g,ec} was determined to be ~2.53 eV, which is quite close to the optically obtained value (E_{g,opt} ~2.48 eV). When we take into account the coulomb repulsive force for the electrochemical band gap, a slightly higher value of (~0.05 eV) E_{g,ec} is reasonable [34].

The normalized emission spectra of the ECL devices at various concentrations (0.5–5 wt%) of **1** are given in Fig. 3a. Regardless of the luminophore content, the maximum wavelength (λ_{max}) of the emitted light was fixed at ~597 nm upon application of 7.5 V_{pp} at 60 Hz. The maximum ECL luminance of each spectrum was plotted as a function of the luminophore concentration (Fig. 3b). A higher maximum luminance appeared with a larger amount of **1**, where the highest luminance was achieved at ~4 wt%. However, the decrease in ECL luminance was observed at ~5 wt% due to the limited solubility of **1** in [EMI][TFSI] (see Fig. S1 in the Supporting Information). With considering similar luminance values (~7.6 Cd/m² at 3 wt% versus ~7.9 Cd/m² at 4 wt%), we chose the optimum composition of 3 wt% for subsequent studies. We



Fig. 2. (a) UV-vis absorption spectrum of the [EMI][TFSI] solution containing **1**. The inset is the enlarged spectrum, in which the onset absorption wavelength is determined. (b) Cyclic voltammogram (CV) for **1** in an acetonitrile (ACN) solution containing 100 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte.

measured the Commission Internationale de l'Eclairage (CIE) 1931 color coordinate (x,y) for the emitted ECL light (Fig. 3c). Coordinates (x,y) of (0.53, 0.45) corresponding to yellow-orange color were extracted, which is similar to those of the reported electroluminescence [20]. The voltage dependence of luminance for ECL devices at various concentrations of **1** was investigated (Fig. 3d). All devices exhibited similar behaviors except for maximum luminance. Namely, irrespective of a luminophore concentration, the turn-on voltage was ~5.5 V_{PP} and the luminance saturation was observed at ~7.5 V_{pp}.

Fig. 4 displays dynamic transient profiles of the applied voltage, device current, and ECL intensity under an AC voltage at three representative frequencies of 60 Hz, 150 Hz, and 500 Hz, respectively. Similar to 2 [35], the ECL devices with 1 also indicated a symmetric emission whenever the voltage switched (see Fig. 4a-c, and Figs. S2-S4 in the Supporting Information). Furthermore, we realized that the period with zero intensity was reduced as the frequency was increased. The effective voltage across the ECL cell is decreased at higher frequency [36]. This may reduce the production of redox species of Ir (ppy)₂(bpy)²⁺ and Ir(ppy)₂(bpy)⁰, leading to shorter emission time. Simultaneously, the duration per cycle also decreases with increasing frequency. However, the time reduction per cycle due to the frequency change is greater than the decrease in the emission time. For example, when the frequency was changed from 150 Hz to 300 Hz, the halfperiod interval decreased by 1.6 ms, but the emission time only decreased by 0.5 ms. As a result, we could observe a shorter non-zero emission period at higher frequencies. This observation implies



Fig. 3. (a) Normalized emission spectra and (b) plots of the maximum ECL luminance of ECL devices at various concentrations of **1**. The luminophore concentration was controlled from 0.5 to 5 wt%. (c) CIE color coordinates (x, y) of the emitted light from the device. The inset image corresponds to the turn-on state, in which the dimensions of the active areas were $2 \text{ mm} \times 2 \text{ mm}$. (d) Voltage dependence of the ECL luminance for ECL devices at three different concentrations of **1**, in which the frequency was fixed at 60 Hz. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

additional possibility for enhancing device luminance by modulating the frequency of applied voltage, which will be discussed shortly.

The time intervals between the current and intensity profiles, corresponding to the response time, were determined and plotted in Fig. 5a. Overall, a similar level ($\sim 0.15 \text{ ms}$) of response time was observed within the experimental frequency range from 30 to 1000 Hz (Fig. 5a). In general, electrical double layers (EDLs) are produced before electrochemical reactions occur. The time required for the formation of EDLs can be estimated from the RC time constant. With considering the cell dimension, ionic conductivity (~10.9 mS/cm) and capacitance ($\sim 7.7 \,\mu\text{F/cm}^2$) of [EMI][TFSI] at room temperature [37], \sim 6.2 µs is calculated, which is much shorter than half period (500 µs) of the highest experimental frequency, 1000 Hz. Moreover, in contrast to DC-driven systems, AC-driven devices do not require long diffusion length of redox species and produce excited luminophores only near the electrode surface. Accordingly, there was no significant difference in kinetics within experimental frequency range of 30-1000 Hz. Ultimately, fast-response ECL devices can be considered more promising candidates in comparison to other representative electrochemical displays such as light emitting electrochemical cells (LECs) that suffer from a slow turn-on response [38–40].

Fig. 5b shows the variations in ECL intensity estimated from the area under ECL profiles within the same period, as a function of frequency. The ECL intensity was enhanced up to 500 Hz as the frequency was increased, which is attributed to the reduced non-zero emission periods [41]. However, the intensity was slightly dropped at 1000 Hz. This phenomenon can be explained by the fact that a smaller amount of excited species were generated within a cycle due to a lower potential difference between two electrodes at higher frequencies [36].

Nonetheless, the number of cycles per unit time was greater at 1000 Hz, so the decrease in luminance was not remarkable.

Because ECL devices are in a nascent stage, there are several properties to be improved for practical purposes. The relatively weak luminance is one representative example. Very recently, we reported an effective strategy to achieve a higher ECL brightness, in which the input AC voltage was tailored by taking into account the electrochemical stability of the redox species [41]. Another methodology has utilized mixed-luminophore systems [13,42], in which the excited species with a relatively higher energy state served as a coreactant. As a result, the concentration of excited species of luminophores having a lower energy state was increased and their light emission became stronger.

Similarly, we added 2 forming energetically higher excited species to the 1-containing ECL system. Fig. 6a shows the changes in emission spectra for the ECL devices when varying the molar ratios between 1 and 2, in which whole amounts of luminophores were fixed. When 60 mol% of 2 was present in the ECL electrolyte, the yellow light emission (~16.6 Cd/m^2) was maximized (see Fig. 6b). In addition to the Ir(ppy)₂(bpy)^{+*} generated via the annihilation route, extra Ir (ppy)₂(bpy)^{+*} can be produced by an electron transfer reaction (equation (9)) between the oxidized $Ir(ppy)_2(bpy)^{\cdot 2+}$ and Ir(diFp $py_{2}(bpy)^{+*}$ formed by its annihilation reaction (namely, equations (6) through (8)). Thus, a greater number of excited $Ir(ppy)_2(bpy)^{+*}$ could be present and a stronger yellow emission was observed. Additionally, we adjusted the frequency of AC voltage applied to the device based on a mixed luminophore system. Fig. 6c exhibits the changes in luminance of the ECL device with varying the voltage frequency. Similar to the 1only device, the maximum luminance ($\sim 27.6 \text{ Cd/m}^2$) was achieved at 500 Hz. Also, a quick response of $\sim\!0.15\,\text{ms}$ was measured at this



Fig. 4. Transient profiles of applied voltage (black, 7.5 V_{pp} square wave), current (red), and ECL intensity (blue) for the ECL devices at a frequency of (a) 60 Hz, (b) 150 Hz, and (c) 500 Hz. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. Frequency dependence of (a) response times, and (b) ECL intensity of ECL devices containing 1, where the voltage was fixed at 7.5 V_{PP}.



Fig. 6. (a) The emission spectra of ECL devices at various molar ratios of 1 and 2, where the total amounts of the luminophores were fixed. (b) Plots of the maximum luminance at $\lambda_{max} \sim 597$ nm of the ECL spectra in (a) as a function of mol % of 1. (c) Plots of luminance of ECL devices versus frequency at an optimal molar ratio between 1 and 2 (40 mol%:60 mol%). (d) Representative transient current (red) and ECL (blue) profiles of the ECL device at 500 Hz. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

optimal frequency (Fig. 6d).

$$Ir(diFppy)_2(bpy)^+ + e^- \rightarrow Ir(diFppy)_2(bpy)^{\cdot 0}$$
(6)

$$Ir(diFppy)_2(bpy)^+ - e^- \rightarrow Ir(diFppy)_2(bpy)^{*2+}$$
(7)

 $Ir(diFppy)_{2}(bpy)^{*0} + Ir(diFppy)_{2}(bpy)^{*2+} \rightarrow Ir(diFppy)_{2}(bpy)^{+*} + Ir (diFppy)_{2}(bpy)^{+}$ (8)

 $Ir(ppy)_2(bpy)^{\cdot 2+} + Ir(diFppy)_2(bpy)^{+*} \rightarrow Ir(ppy)_2(bpy)^{+*} + Ir(diFppy)_2(bpy)^{\cdot 2+}$ (9)



Fig. 7. Summary of strategies employed in this work to improve ECL brightness. Inset images correspond to photographs for the 1-only device at 60 Hz (left), and the device based on a mixed luminophore at 500 Hz (right). The operating voltage was fixed at 7.5 $V_{\rm PP}$.

Fig. 7 depicts the strategies utilized in this work. Although the luminophore 1 successfully worked in ECL systems, the luminance (\sim 7.6 Cd/m²) was low at the conventional operating condition (i.e. 60 Hz). Therefore, we employed mixed luminophore systems for additionally generating excited species through the coreactant path and controlled applied frequency. As a result, the luminance (\sim 27.6 Cd/m²) of the emitted yellow light via ECL was increased \sim 3.5 times.

4. Conclusions

In conclusion, we proposed the use of **1** as a yellow emitting ECL luminophore and demonstrated ECL devices based on [EMI][TFSI] and **1**. The devices exhibited a fast response (~0.15 ms) to the stimulation of symmetric AC square waves of 7.5 V_{pp}, irrespective of the voltage polarization rate. The improvement in ECL intensity could be achieved by utilizing **2** as a coreactant, which leads to the formation of extra Ir (ppy)₂(bpy)^{+*} through the coreactant pathway in addition to the general annihilation pathway. Additionally, we achieved higher luminance by adjusting the frequency of applied AC voltage input. It is anticipated that the development of new ECL materials capable of directly emitting various colors other than RGB can expand the functionality of ECL displays.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

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