

Efficient Red Phosphorescent Electrogenerated Chemiluminescence Cell Based on a Combination of an Iridium Complex and a Carbazolyl Dicyanobenzene Derivative



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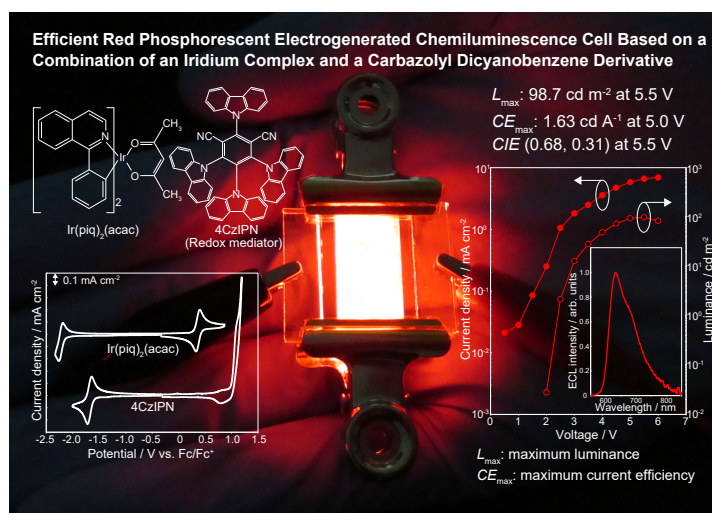
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ABSTRACT

An efficient red phosphorescent electrogenerated chemiluminescence (ECL) cell was successfully designed by utilizing a cyclometalated iridium(III) complex and a carbazolyl dicyanobenzene derivative. The ECL solution, which contained bis(1-phenylisoquinoline)(acetylacetonate)iridium(III) ($\text{Ir}(\text{piq})_2(\text{acac})$) as a luminescent material and 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as a redox mediator, was prepared and injected in a microfluidic ECL cell. The cell, which consisted of the 5- μm -thick microchannels sandwiched between transparent electrode pairs with the prepared solution, exhibited a saturated red emission with Commission Internationale de l'Éclairage (CIE) coordinates of (0.68, 0.31), a maximum luminance of 98.7 cd m^{-2} , and a maximum current efficiency of 1.63 cd A^{-1} . Photophysical and electrochemical studies were also carried out to support our experimental results.



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Keywords : Electrogenerated Chemiluminescence, Phosphorescent Iridium Complex, Redox Mediator, Microfluidic ECL Cell

1. Introduction

Cyclometalated iridium(III) complexes have been widely used as the guest emitter to design highly efficient organic light-emitting diodes (OLEDs) because they are capable of harvesting both singlet and triplet excited states (S_1 and T_1), which are electrically generated in a ratio of 1 : 3, for light emission.^{1–4} The strong spin-orbit coupling induced by the iridium(III) center allows an intersystem crossing from S_1 to T_1 , leading to phosphorescence (radiative relaxation) from T_1 to a singlet ground state (S_0) at room temperature. In particular, the iridium(III) complexes with bis- or tris-1-phenylisoquinoline (piq) ligands are well-known red phosphorescent materials, and OLEDs with these complexes have been reported to exhibit a saturated red emission close to the national television standard committee (NTSC) red coordinates of (0.67, 0.33).^{4–10}

Recently, electrogenerated chemiluminescence (ECL) cells have drawn attention due to their potential applications in unique

displays.^{11–15} The typical ECL cell employs a simple structure of the luminescent solution sandwiched between two transparent electrodes, whereas OLEDs are based on the organic multilayered film structure. In general, the ECL solutions for the sandwich cells have been made by dissolving one kind of the luminescent material such as 9,10-diphenylanthracene (DPA) for blue, 5,6,11,12-tetraphenyltetraene (rubrene) for yellow, and phosphorescent ruthenium complexes for orange-red in an organic solvent, which is called the single ECL systems. In this system, the excited molecule is produced by an electron transfer reaction between the radical anion and cation (reduced and oxidized species) generated from the same parent material. Thus, the luminescent material needs to be both oxidized and reduced in a well-balanced manner. Although, electrochemical properties and ECL phenomena of the phosphorescent iridium(III) complexes have been widely studied by many researchers in a three-electrode system (working, counter, and reference electrodes),^{16–20} they have not been actively employed in the sandwich cells yet.

In 2023, we proposed the mixed ECL systems using a redox mediator for the sandwich cells, and the performances of a yellow fluorescent ECL cell were found to be significantly improved by

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adding a stilbene derivative as the mediator to the rubrene solution.²¹ A maximum luminance ($L_{\max}$) of 292 cd m^{-2} and a maximum current efficiency ($CE_{\max}$) of 4.50 cd A^{-1} were obtained by this system. Furthermore, in 2024, we also developed an iridium(III) complex-based yellow phosphorescent ECL cell with the $L_{\max}$ of over 100 cd m^{-2} and the $CE_{\max}$ of 2.84 cd A^{-1} .²² In that work, the solution was prepared by dissolving bis(2-phenylbenzothiazolato)(acetylacetonate)iridium(III) ($\text{Ir}(\text{BT})_2(\text{acac})$), which is frequently used as a yellow emitter for white OLEDs,²³ as the luminescent material and 4,5-bis(carbazol-9-yl)-1,2-dicyanobenzene (2CzPN), which is a well-known sky-blue emitter, as the mediator in the solvent. Cyclic voltammetry (CV) measurements revealed that the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) levels of 2CzPN (-5.8 and -3.0 eV) were both considerably deeper than those of $\text{Ir}(\text{BT})_2(\text{acac})$ (-5.2 and -2.5 eV). Furthermore, $\text{Ir}(\text{BT})_2(\text{acac})$ was found to have a relatively shallow LUMO level. Thus, we considered that in the sandwich cell, the radical anion of 2CzPN ($2\text{CzPN}^{\cdot-}$) and the radical cation of $\text{Ir}(\text{BT})_2(\text{acac})$ ($\text{Ir}(\text{BT})_2(\text{acac})^{\cdot+}$) were generated preferentially, and consequently, the excited $\text{Ir}(\text{BT})_2(\text{acac})$ molecules were efficiently produced by the electron transfer reaction between them.

The display screens have been generally composed of the subpixels of the three primary colors (red, green, and blue) to give the full range of colors. Thus, the development of efficient sandwich ECL cells with high color purity for the three primary colors is a big challenge for future ECL-based displays. In this study, we propose a novel red phosphorescent cell based on $\text{Ir}(\text{piq})_2(\text{acac})$ by referring to the above-mentioned yellow phosphorescent cell. In OLED studies, a carbazoyl dicyanobenzene derivative, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) is one of the most famous green thermally activated delayed fluorescent (TADF) material and has been reported to have a deep LUMO level and act as an electron trapping site in a host material.^{24,25} Thus, in this study, 4CzIPN was employed as the redox mediator which accepts an electron from the cathode and donates it to the radical cation of $\text{Ir}(\text{piq})_2(\text{acac})$. The microfluidic ECL cell was used in order to evaluate the proposed solution.

2. Experiment

2.1 Fabrication and evaluation of microfluidic ECL cells

Figure 1 shows a photo of the microfluidic ECL cell and chemical structures of $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN. The cell, whose fabrication process was similar to that described in our previous work,^{26,27} has a sandwich structure consisting of 5- μm -thick SU-8 microchannels, an indium tin oxide (ITO) anode-patterned polyethylene terephthalate (PET) film, and a fluorine-doped tin oxide (FTO) cathodes-patterned glass. The cells with three types of the solutions (Devices A, B, and C) were fabricated and evaluated in ambient air. Device A has a solution containing 2 mM ($M = \text{mol L}^{-1}$) $\text{Ir}(\text{piq})_2(\text{acac})$ and 4 mM 4CzIPN. Device B has a solution containing 2 mM $\text{Ir}(\text{piq})_2(\text{acac})$. Device C has a solution containing 4 mM 4CzIPN. Here, we used a mixed solvent of acetonitrile and 1,2-dichlorobenzene in the ratio of 1 : 2 (v/v) with 180 mM 1,2-diphenoxyethane as an ion conductive assist dopant.¹¹ The prepared solutions were subsequently injected into the microchannel sandwiched by the electrode pair via capillary force. The cells were operated with a direct current (DC) voltage under the stopped flow condition, and their performances were measured from the PET side. The ECL spectra were obtained with a multichannel spectrometer (Ocean Optics, Flame-S), while the current density–voltage–luminance (J – V – L) characteristics were measured using a source meter (Keithley, model 2400) with a luminance meter (Konica Minolta, LS-160).

2.2 Photophysical and electrochemical studies

The sample solutions for the photophysical and electrochemical

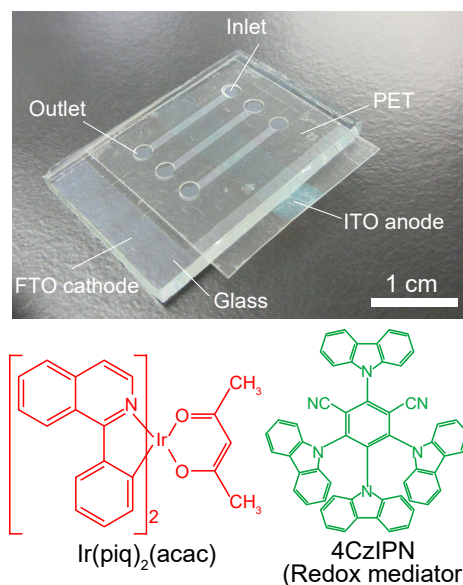


Figure 1. Photo of the microfluidic ECL cell and chemical structures of $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN.

measurements were also prepared in the mixture of acetonitrile and 1,2-dichlorobenzene (1 : 2 (v/v)). An ultraviolet-visible (UV-vis) spectrophotometer (Hitachi, U-5100) was used for acquiring absorption spectra, while the photoluminescence (PL) emission spectra were obtained using a spectrofluorometer (Shimadzu, RF-6000).

The CV measurements were conducted at a scan rate of 100 mV s^{-1} with an electrochemical analyzer (BAS, ALS600E). The three-electrodes system, which includes a glassy carbon disk working electrode (diameter, 1 mm), a platinum wire coil counter electrode, and a silver wire reference electrode, was used, and tetrabutylammonium hexafluorophosphate (TBAPF_6) was added to the solution as a supporting electrolyte at a concentration of 100 mM. All redox potentials were referenced to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

3. Results and Discussion

Figure 2 shows the normalized UV-vis absorption and PL spectra of $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN in the mixed solvent. The photos of both the solutions under a 365 nm UV lamp are also presented in the inset. The concentration of both $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN for the PL measurements was 0.1 mM. A strong absorption band of $\text{Ir}(\text{piq})_2(\text{acac})$ (at the concentration of $12.5 \mu\text{M}$) at around 298 nm was reported to be assigned to spin-allowed ligand-centered (LC) transitions (π – π^*).⁵ In addition, a weak absorption band in the range of 350–500 nm was attributed to singlet and triplet metal-to-ligand charge transfer transitions ($^1\text{MLCT}$ and $^3\text{MLCT}$). The maximum PL peak ($\lambda_{\text{PL,max}}$) of $\text{Ir}(\text{piq})_2(\text{acac})$ was measured at 630 nm (red light emission), which is ascribed to the excited $^3\text{MLCT}$ state.⁵ 4CzIPN (at $20 \mu\text{M}$) showed the strong absorption bands at 326 nm and 368 nm, which corresponds to the CT transition from the carbazoyl donor unit to the dicyanobenzene acceptor unit.²⁸ The yellowish-green emission was observed from the 4CzIPN solution, and its $\lambda_{\text{PL,max}}$ was at 552 nm.

Figure 3 shows the CV characteristics of $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN. $\text{Ir}(\text{piq})_2(\text{acac})$ was found to show distinct cathodic reduction and anodic oxidation waves in a potential range of -2.33 to 0.86 V vs. Fc/Fc^+ , suggesting that its radical anion and cation ($\text{Ir}(\text{piq})_2(\text{acac})^{\cdot-}$ and $\text{Ir}(\text{piq})_2(\text{acac})^{\cdot+}$, respectively) are both stable. These reduction and oxidation waves were reported to be

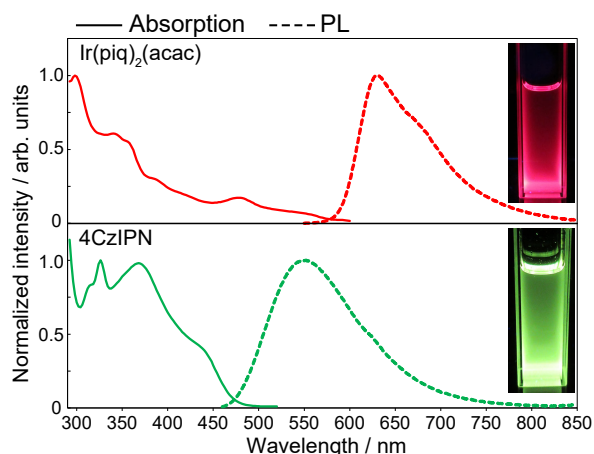


Figure 2. Normalized UV-vis absorption and PL spectra of Ir(piq)₂(acac) and 4CzIPN in the mixed solvent. The insets are photos of both the solutions under a 365 nm UV lamp.

attributed to the reduction of the piq ligand and the oxidation of the iridium(III) center, respectively.⁵ The reduction and oxidation onset potentials ($E_{\text{on}}^{\text{Red}}$ and $E_{\text{on}}^{\text{Ox}}$) were -2.15 and 0.29 V vs. Fc/Fc⁺, respectively, while the reduction and oxidation midpoint potentials ($E_{\text{m}}^{\text{Red}}$ and E_{m}^{Ox}) were -2.22 V and 0.36 V vs. Fc/Fc⁺, respectively. It can be seen that 4CzIPN is more readily reduced and more difficult to be oxidized than Ir(piq)₂(acac). In other words, the HOMO and LUMO levels of the neutral 4CzIPN are both deeper than those of the neutral Ir(piq)₂(acac), as shown in the inset of Fig. 3. In the potential range of -2.00 to 1.19 V vs. Fc/Fc⁺, although 4CzIPN showed a distinct cathodic reduction, an irreversible oxidation wave was observed in the anodic scan. It has been reported that the cathodic reduction wave corresponds to the reduction of the dicyanobenzene acceptor unit, while the anodic oxidation wave corresponds to the oxidation of the carbazolyl donor unit.²⁸ As judged from the CV of 4CzIPN, its radical anion (4CzIPN^{•−}) was stable, whereas its radical cation (4CzIPN^{•+}) was significantly unstable. The $E_{\text{on}}^{\text{Red}}$ and $E_{\text{on}}^{\text{Ox}}$ for 4CzIPN were -1.60 and 1.00 V vs. Fc/Fc⁺, respectively, while its $E_{\text{m}}^{\text{Red}}$ was -1.68 vs. Fc/Fc⁺. The photophysical and electrochemical properties of two molecules are summarized in Table 1. The HOMO and LUMO levels were estimated from the $E_{\text{on}}^{\text{Ox}}$ and $E_{\text{on}}^{\text{Red}}$ values and the ionization energy of ferrocene (4.8 eV below the vacuum level).²⁹ The HOMO-LUMO energy gap of the neutral 4CzIPN was found to be larger than that of the neutral Ir(piq)₂(acac). We also measured the CVs of Ir(piq)₂(acac) and 4CzIPN in a wide potential range. The onset of the second oxidation potential for Ir(piq)₂(acac) was observed at around 1.06 V vs. Fc/Fc⁺, which is more than 0.7 V vs. Fc/Fc⁺ higher than the $E_{\text{on}}^{\text{Ox}}$ of the neutral Ir(piq)₂(acac). This suggests that the HOMO and singly occupied molecular orbital (SOMO) levels of Ir(piq)₂(acac)^{•+} are significantly deeper than the HOMO level of the neutral Ir(piq)₂(acac). In addition, the dication of Ir(piq)₂(acac) (Ir(piq)₂(acac)²⁺) was found to be unstable from the CV experiments. In a

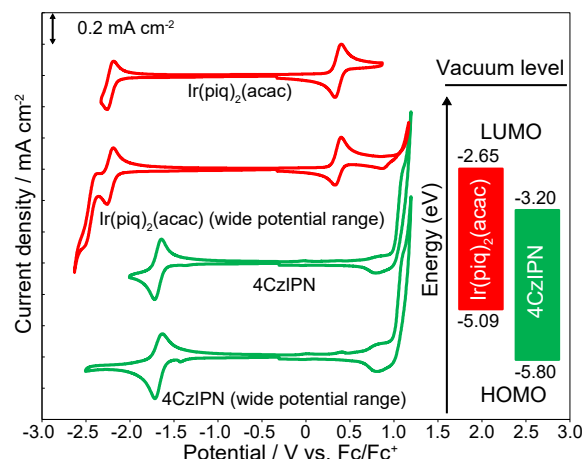


Figure 3. CVs of Ir(piq)₂(acac) (1 mM) and 4CzIPN (1 mM) at a scan rate 100 mV s^{-1} . The inset shows the HOMO and LUMO levels calculated from the redox onset potentials and the ionization energy of ferrocene (4.8 eV).

negative scan direction, Ir(piq)₂(acac) exhibited two successive reduction waves. First and second waves may correspond to the reduction from the neutral state to Ir(piq)₂(acac)^{•−} and from Ir(piq)₂(acac)^{•−} to the dianion (Ir(piq)₂(acac)^{2−}), respectively. This suggests that the LUMO level of the neutral Ir(piq)₂(acac) and the LUMO or SOMO level of Ir(piq)₂(acac)^{•−} are close to each other. Ir(piq)₂(acac)^{2−} was found to be somewhat unstable. In contrast, even when a high negative potential (up to -2.50 V vs. Fc/Fc⁺) was applied to 4CzIPN, its second reduction wave was not observed, suggesting that the LUMO and SOMO levels of 4CzIPN^{•−} are significantly shallow in comparison with the LUMO level of the neutral 4CzIPN.

Figure 4a shows the J - V - L (main plot) and current efficiency- V (inset plot) characteristics of Device A. Its turn-on voltage (defined as luminance of above 0.01 cd m^{-2}) was 2.0 V, and both the current density and luminance increased stably with the increase in the applied voltage. Device A showed the L_{max} of 98.7 cd m^{-2} at 5.5 V and the CE_{max} of 1.63 cd A^{-1} at 5.0 V. Tris(2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate) (Ru(bpy)₃(PF₆)₂), which emits orange-red light, is one of the most studied materials for the sandwich cells, and many researchers have investigated to improve their performances by using the methods such as the alternating current (AC)-driven technique and the metal oxide nanoparticles coating on one electrode.^{12–15} The L_{max} of Device A was found to be comparable to that of the Ru(bpy)₃²⁺-based cell.^{12,15,26} Furthermore, its CE_{max} was the highest among the reported reddish ECL cells. Figure 4b shows the ECL spectra of Device A at different voltages from 3.0 to 5.5 V and the photo of Device A at 5.5 V. The obtained spectra were identical to each other and also to the PL spectrum of Ir(piq)₂(acac) (see also Fig. 2). These results indicate that the T₁ state of Ir(piq)₂(acac) was efficiently produced in Device A. In addition, the Commission Internationale de l'Éclairage (CIE)

Table 1. Photophysical and electrochemical properties.

Sample	$\lambda_{\text{Abs,max}}^a$ /nm	$\lambda_{\text{PL,max}}^a$ /nm	$E_{\text{on}}^{\text{Red } a,b}$ /V	$E_{\text{on}}^{\text{Ox } a,b}$ /V	$E_{\text{m}}^{\text{Red } a,b}$ /V	$E_{\text{m}}^{\text{Ox } a,b}$ /V	LUMO ^c /eV	HOMO ^c /eV	E_{g}^d /eV
Ir(piq) ₂ (acac)	298	630	-2.15	0.29	-2.22	0.36	-2.65	-5.09	2.44
4CzIPN	326	552	-1.60	1.00	-1.68	N.D.	-3.20	-5.80	2.60

^a Measured in a mixture of acetonitrile and 1,2-dichlorobenzene (1 : 2 (v/v)) at room temperature. ^b vs. Fc/Fc⁺. ^c Calculated from the redox onset potentials of the employed material and the ionization energy of ferrocene (4.8 eV). ^d Determined by the difference between the redox onset potentials. N.D. = not determined.

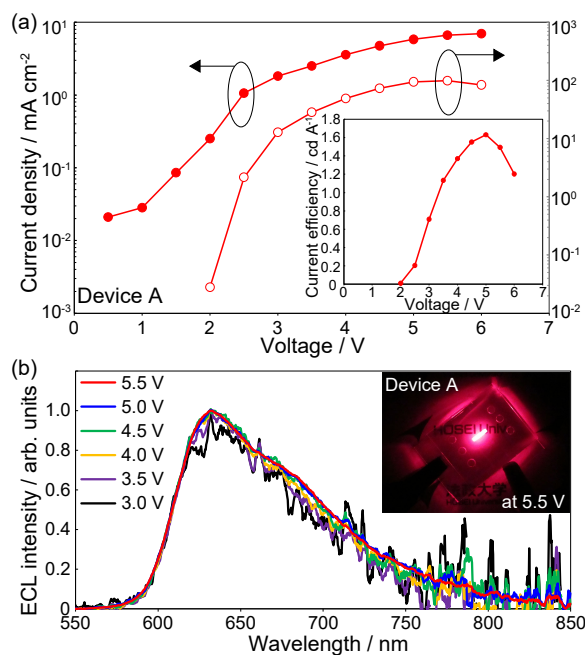


Figure 4. (a) J - V - L and CE - V (inset) characteristics of Device A. (b) ECL spectra at the voltages from 3.0 to 5.5 V and a photo of Device A at 5.5 V (inset).

coordinates of (0.68, 0.31) were obtained when the voltage of 5.5 V was applied to Device A, which is very close to the NTSC red coordinates of (0.67, 0.33). Thus, we can conclude that a bright, efficient, and pure red sandwich ECL cell was successfully demonstrated for the first time by combining $\text{Ir}(\text{piq})_2(\text{acac})$ with 4CzIPN.

Figure 5 shows the J - V - L characteristics of Devices B and C. The turn-on voltage of both the cells was 3.0 V, which is 1.0 V higher than that of Device A. Furthermore, their luminance values were significantly low in comparison with Device A. Devices B showed the luminance of 0.26 cd m^{-2} at 5.5 V, and its ECL spectrum was not clearly detected by the multichannel spectrometer. In the case of Device B, it was also found that although the current density increased gradually with the increase in the applied voltage, the luminance value did not increase at the voltage higher than 4.0 V. Device C exhibited the L_{max} of 4.11 cd m^{-2} at 5.5 V, and its ECL spectrum shown in the inset of Fig. 5b was almost identical to the PL spectrum of 4CzIPN. The reason why these cells exhibited high turn-on voltage and low luminance can be attributed to the unbalanced radical anion and cation generation in the solution. In Device B, $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ may be more preferentially generated by the hole injection from the anode than $\text{Ir}(\text{piq})_2(\text{acac})^{-}$ at the low voltage (below 3.0 V) because the HOMO and LUMO levels of the neutral $\text{Ir}(\text{piq})_2(\text{acac})$ are both shallow. The solution maybe contain oxygen (since the devices were fabricated in ambient air) and impurities which can be reduced easier than $\text{Ir}(\text{piq})_2(\text{acac})$ having a negatively high reduction potential. Thus, the reductions of impurities and also solvent were considered to occur on the cathode surface at the low voltage. At the high voltage (above 4.0 V), unstable $\text{Ir}(\text{piq})_2(\text{acac})^{2-}$ and $\text{Ir}(\text{piq})_2(\text{acac})^{2+}$ may be generated on the cathode and anode surfaces, respectively, because of the electrochemical characteristics of $\text{Ir}(\text{piq})_2(\text{acac})$ (see also Fig. 3). Thus, we expect that Device B having low luminescent characteristics at the high voltage was attributed to the formation of $\text{Ir}(\text{piq})_2(\text{acac})^{2-}$ and $\text{Ir}(\text{piq})_2(\text{acac})^{2+}$. In Device C, the excited 4CzIPN molecules were not generated sufficiently because 4CzIPN^{+} was significantly unstable (see Fig. 3) and presumably polymerized on the anode surface.²⁸

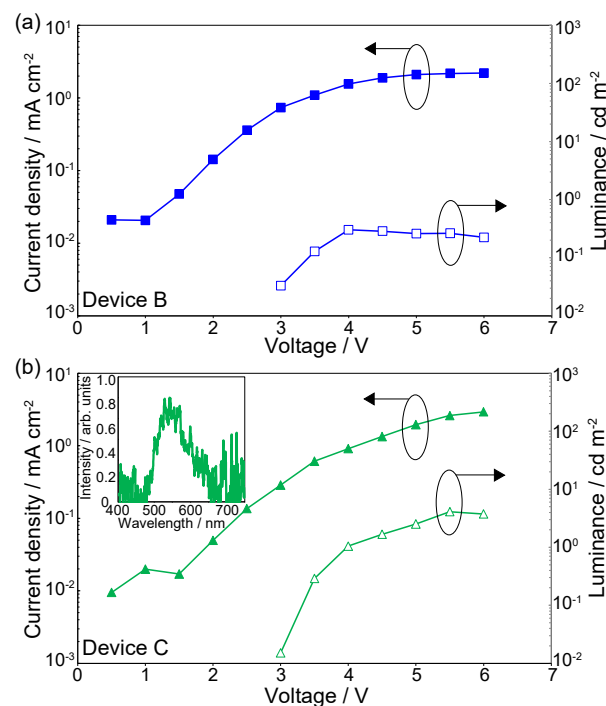


Figure 5. J - V - L characteristics of Devices (a) B and (b) C. The inset of (b) is the ECL spectrum of Device C at 5.5 V.

From here on, we will focus on the light emission process of Device A which has both $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN. From the results of the J - V - L measurements of Devices B and C, in the case of Device A, $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ and 4CzIPN^{-} were expected to be both generated in the solution. Therefore, the excited $\text{Ir}(\text{piq})_2(\text{acac})$ is plausibly produced as the result of the collision of $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ and 4CzIPN^{-} . From the viewpoint of the frontier orbital levels of the neutral $\text{Ir}(\text{piq})_2(\text{acac})$ and 4CzIPN shown in the inset of Fig. 3, the transfer of an electron from the SOMO of $4\text{CzIPN}^{\cdot-}$ (-3.20 eV) to the LUMO of $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ (-2.65 eV) is found to be an energetically unfavorable uphill reaction ($+0.55 \text{ eV}$). In addition, the HOMO-LUMO energy gap of the neutral $\text{Ir}(\text{piq})_2(\text{acac})$ (2.44 eV) (see Table 1) is larger than the T_1 emissive energy of $\text{Ir}(\text{piq})_2(\text{acac})$ (630 nm , ca. 1.97 eV) (see Fig. 4b). This suggests that the direct electron injection into the LUMO level of $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ is not necessary to produce the T_1 state of $\text{Ir}(\text{piq})_2(\text{acac})$. Recently, in the field of OLEDs, the CT complexes have attracted attention for developing low operating voltage and highly efficient fluorescent devices.^{30–33} Those OLED devices mainly consist of an electron donor layer, which also serves as the fluorescent emitter, and an electron acceptor layer. The excited CT complex is formed at the interface between the donor and acceptor layers, and then the T_1 state of the donor is generated by the electron transfer from the excited CT complex to the donor.^{32,33} Finally, the S_1 state of the donor is produced by triplet-triplet annihilation. Thus, in Device A, it is likely that the excited CT complex was formed between $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ and 4CzIPN^{-} , and consequently, the T_1 state of $\text{Ir}(\text{piq})_2(\text{acac})$ was formed by the electron transfer reaction between the CT complex and $\text{Ir}(\text{piq})_2(\text{acac})^{+}$.

On the other hand, in quantum chemical calculations, it has been reported that the frontier orbital levels of some aromatic hydrocarbons and metal-organic oligomers are changed when their neutral state converts to the radical ion state.^{34–36} The frontier orbital levels of the radical anion and cation have been shown to be shallower and deeper, respectively, than those of the neutral molecule.³⁶ From the above-mentioned results of the wide potential range CV scans (Fig. 3), the SOMO level of $\text{Ir}(\text{piq})_2(\text{acac})^{+}$ may be deeper than the

HOMO of the neutral $\text{Ir}(\text{piq})_2(\text{acac})$, while the SOMO level of $4\text{CzIPN}^{\cdot-}$ may be shallower than the LUMO of the neutral 4CzIPN . Thus, in Device A, the SOMO level of $4\text{CzIPN}^{\cdot-}$ is likely to become shallower than the LUMO level of $\text{Ir}(\text{piq})_2(\text{acac})^{\cdot+}$, leading to the generation of the excited $\text{Ir}(\text{piq})_2(\text{acac})$ and the ground state of 4CzIPN by the electron transfer from the SOMO of $4\text{CzIPN}^{\cdot-}$ to the LUMO $\text{Ir}(\text{piq})_2(\text{acac})^{\cdot+}$. To be able to figure out this light emission process, more advanced studies are needed. In particular, a relationship between the frontier orbital levels of $\text{Ir}(\text{piq})_2(\text{acac})^{\cdot+}$ and $4\text{CzIPN}^{\cdot-}$ must be clarified quantitatively. We consider that the LUMO level and the SOMO (or HOMO)-LUMO energy gap of $\text{Ir}(\text{piq})_2(\text{acac})^{\cdot+}$ may be revealed by UV-vis spectroelectrochemical measurements.³⁷ In the future, we will also carry out quantum chemical calculations for the frontier orbital levels of the employed materials to support to our experimental results. In addition, in Device A, an energy transfer may occur from the excited 4CzIPN to the neutral $\text{Ir}(\text{piq})_2(\text{acac})$ because the ECL spectrum of Device C overlaps with the MLCT absorption spectrum of $\text{Ir}(\text{piq})_2(\text{acac})$ (see Figs. 2 and 5b).

4. Conclusions

The pure red phosphorescent ECL cell with the CE_{max} of 1.63 cd A^{-1} was constructed by introducing 4CzIPN to the $\text{Ir}(\text{piq})_2(\text{acac})$ solution. The cell with the proposed solution (Device A) exhibited a bright red emission derived from the excited $\text{Ir}(\text{piq})_2(\text{acac})$, and the obtained CIE coordinates of (0.68, 0.31) at 5.5 V were very close to the standard red CIE coordinates of (0.67, 0.33) required by NTSC. In addition, the luminance of 98.7 cd m^{-2} was achieved at 5.5 V in Device A, which was about 300 times higher than that of the cell in the absence of 4CzIPN (Device B) at the same voltage. However, the luminescent performances of the developed cell have lagged behind those of the solid-state OLEDs. Thus, we will continue to deepen the research on the mixed ECL systems using several redox mediators. In preliminary tests, instead of 4CzIPN , we added 2CzPN to the $\text{Ir}(\text{piq})_2(\text{acac})$ solution as the redox mediator, and the red ECL emission derived from $\text{Ir}(\text{piq})_2(\text{acac})$ was also observed from the microfluidic ECL cell. We will evaluate the effect of the reduction potential (LUMO level) of the redox mediator materials on the ECL performances of the $\text{Ir}(\text{piq})_2(\text{acac})$ -based cell.

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CRedit Authorship Contribution Statement

Manaka Kobayashi: Data curation (Lead), Formal analysis (Lead), Investigation (Lead), Writing – original draft (Lead)
 Nobuhiko Akino: Data curation (Lead), Formal analysis (Lead), Investigation (Lead), Writing – review & editing (Equal)
 Hiro Chatani: Formal analysis (Equal), Investigation (Equal)
 Jun Mizuno: Resources (Equal), Writing – review & editing (Equal)
 Ryoichi Ishimatsu: Formal analysis (Lead), Writing – review & editing (Lead)
 Takashi Kasahara: Conceptualization (Lead), Data curation (Equal), Formal analysis (Lead), Funding acquisition (Lead), Investigation (Supporting), Methodology (Lead), Supervision (Lead), Writing – original draft (Lead)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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