Efficient Electrogenerated Chemiluminescence from Bis-Cyclometalated Iridium(III) Complexes with Substituted 2-Phenylquinoline Ligands

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The ECL behavior of bis-cyclometalated $(pq)_2Ir(LX)$ complexes, in which pq is a 2-phenylquinoline anion and LX is a monoanionic bidentate ligand (e.g., acetylacetonate, picolinate, etc.), and the specific influences of the electrochemical stability and photoluminescence quantum yield (PL QY) of luminophores on ECL generation have been investigated. In this study, efficient ECLs, some of which even approached $\Phi_{ECL} = 0.88$ (18× higher than that of $Ru(bpy)_3{}^{2+}$), have been observed in the annihilation process. The simultaneous accumulation to excited singlet S_1 and triplet T_1 states and the spin−orbit coupling characteristics of transition metal complexes are expected to produce efficient annihilation ECL, which permits the high efficiency to exceed PL QY. A cyclic voltammetric study has revealed that the ECL intensity depends primarily on the electrochemical stability of the redox precursors of $(pq)_2Ir(LX)$s. For example, $(pq)_2Ir(acac)$ (acac = acetylacetonate anion), which shows irreversible reduction, has produced efficient ECL during the oxidative−reductive process but less intense ECL during both the annihilation and reductive−oxidative processes. In the oxidative−reductive process, $(pq)_2Ir(LX)$s also produces efficient ECL reacting with tri-*n*-propylamine radical precursors (TPA$^{\prime\bullet}$). During the oxidative−reductive process, $(pq)_2Ir(LX)$/TPA couples undergo many competitive pathways involving both heterogeneous and homogeneous reactions. The tendency of ECL intensities with respect to their PL QYs is more complicated than that in the case of the annihilation process. These findings provide useful information on the fundamental ECL studies and the search for new ECL luminophores or practical ECL applications, such as analysis based on ECL and electroluminescent devices.

Introduction

Electrogenerated chemiluminescence (ECL) is the emission of light from the electron-transfer reaction between electrochemically generated precursors in the vicinity of an electrode.[1−3] ECL contains information on both the kinetics of the heterogeneous electrode processes and the subsequent homogeneous chemical reactions in solution. In practice, the emission is controlled by electronic on/off switching at an easily attainable potential; therefore, ECL has attracted attention as an interesting methodology for practical applications, such as chemical anaysis.[1,2,4,5] Since Bard's group first reported on ECL from tris-(2,2′-bipyridyl) ruthenium(II), $Ru(bpy)_3{}^{2+}$, in 1972,[6] $Ru(bpy)_3{}^{2+}$ derivatives have been studied as the important ECL luminophore for decades. An ECL system that contains $Ru(bpy)_3{}^{2+}$ and tri-*n*-propylamine (TPA) as a coreactant provides a highly sensitive bioanalytical methodology for pharmaceutical, clinical, and environmental applications.[7−15] Commercialized ECL systems with $Ru(bpy)_3{}^{2+}$ (or its derivatives) have been utilized in analytical methods for immunoassays and DNA determinations.[16−19]

Transition metal complexes with high photoluminescence quantum yields (PL QYs) are usually expected to exhibit intense ECL. For example, $Ru(bpy)_3{}^{2+}$ with an ECL efficiency of $\Phi_{ECL} = 0.05$ produces an emitting charge-transfer triplet with an efficiency that approaches unity and is comparable with photoluminescence data of $\Phi_{PL} = \sim0.05$.[20,21] The search for new ECL luminophores whose ECL performance is higher than that of a conventional $Ru(bpy)_3{}^{2+}$ system is still an important topic in ECL studies. Much of the literature on the complexes

is concerned with several types of coordination compounds, such as Ru(II),[22,23] Os(II),[24] trischelate (with 2,2′-bipyridine or 1,-10-phenanthroline as the chelating ligand), binuclear Ir(I) complex,[25] and Mo(II) halide clusters.[26] Recently, the materials used for organic light-emitting diodes (OLEDs, i.e., Al(III) trischelate,[27] Pt(II),[28] and cyclometalated Ir(III) trischelate[28,29]) have been studied as new ECL luminophores. Among various transition metal complexes, cyclometalated Ir(III) trischelates, which exhibit high PL QYs and stable redox characteristics, have attracted attention as promising materials for ECL studies. Tris(2-phenylpyridine)iridium(II) complex, $Ir(ppy)_3$, having an excellent luminescence property with a very high efficiency ($\Phi_{PL} = \sim0.4$) and a nice electrochemical stability at room temperature, shows intense ECL via the annihilation reaction between its redox precursors.[29−32] In our previous report,[31] we have proposed the production of highly efficient ECL from cyclometalated iridium(III) complexes by controlling the thermodynamic parameters between a luminophore and TPA to enhance the population of the excited luminophore and have suggested how to design an efficient ECL system by modifying the redox parameters of the luminophore.

This report describes ECL systems based on cyclometalated iridium(III) complexes (bis-cyclometalated complexes whose general formula is $(pq)_2Ir(LX)$, where (pq) is a 2-phenylquino-line anion (Figure 1)) in order to understand ECL efficiency in more detail and elucidate the roles of the electrochemical and photophysical characteristics. Quantitative studies on ECL are performed in the following three processes: (i) annihilation, redox pulsing process on $(pq)_2Ir(LX)^{\bullet+}/(pq)_2Ir(LX)^{\bullet-}$; (ii) oxidative−reductive process, TPA-assisted ECL; and (iii) reductive−

ECL of Bis-Cyclometalated (pq)2Ir(LX) Complexes

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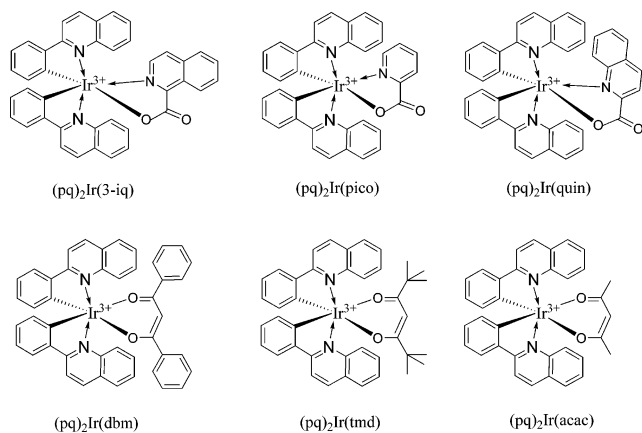
Figure 1. Structure of bis (2-phenylquinoline) iridium(III) (LX) complexes. LX in (pq)$_2$Ir(LX) corresponds to (3-iq), 3-isoquinaldate anion; (pico), picolinate anion; (quin), quinaldate anion; (dbm), dibenzoylmethane anion; (tmd), 2,2′,6,6′-tetramethylhepta-3,5-dione anion; and (acac), acetylacetonate anion.

oxidative process, S$_2$O$_8^{2-}$-assisted ECL. A very high ECL efficiency is obtained with (pq)$_2$Ir(pico) in the annihilation process, and it exceeds the PL QY of the luminophore. These results are discussed in relation with the direct population of triplet T$_1$, and singlet S$_1$ excited states and the spin−orbit coupling of the central heavy metal ion during electrochemical excitation. The electrochemical stability of their radical ions (i.e., (pq)$_2$Ir(LX)$^{•+}$ or (pq)$_2$Ir(LX)$^{•-}$) also has a significant influence on the efficient emission in the ECL processes. Some (pq)$_2$Ir(LX)s, which exhibit reversible electrochemical behavior during both the oxidative and reductive processes, produce efficient emissions in the three types of ECL processes. Furthermore, the ECL produced by all (pq)$_2$Ir(LX)/TPA couples is more intense than that produced by the Ru(bpy)$_3^{2+}$ system. To the best of our knowledge, this is the first report on extremely high ECL efficiencies, even up to Φ_{ECL} = 0.88. These results provide extensive information for future ECL studies and an efficient ECL system for analytical applications.

Experimental Section

Absorbance and Photoluminescence. UV−visible spectra were measured using a Scinco 2100 spectrophotometer (Scinco Co., Seoul, Korea). Photoluminescence spectra were obtained using a Jasco FP-7500 spectrofluorometer (Jasco Co., Tokyo, Japan). The excitation wavelength was 440 nm for (pq)$_2$Ir(LX), and PL detection was made in the range of 455−730 nm (λ_{PL} = 502 nm). The relative photoluminescence efficiencies of (pq)$_2$Ir(LX) in a dichloromethane solution (degassed by several freeze-and-thaw cycles) were measured by the optical dilute method using bis(2-(p-tolyl)pyridinato-N, C$^{2'}$) (picolinate) iridium(III), (tpy)$_2$Ir(acac) in the dichloromethane (Φ_{PL} = 0.31) solution as a relative reference.[33]

Electrochemistry and Electrogenerated Chemiluminescence. Cyclic voltammetry (CV) was performed using a CH Instruments 660 Electrochemical Analyzer (CH Instruments, Inc., Texas). All electrochemical and ECL experiments were referenced with respect to a Ag wire quasireference electrode (AgQRE). All potential values were calibrated against the standard calomel electrode (SCE) by adding ferrocene as an internal reference ($E°$(Fc$^+$/Fc) = 0.424 V vs SCE).[34] A stepwise potential for ECL experiments was generated using a Voltalab PGZ 402 Radiometer (Radiometer Analytical SAS, Lyon, France). In the annihilation ECL experiments, a two-step potential of 10 Hz was applied with 0.2 V more than the redox

potentials of the complexes added. In oxidative−reductive ECL, a 10-Hz stepwise potential from 0.1 to 1.9 V was applied to the (pq)$_2$Ir(LX)/TPA system because the maximum ECL intensity was usually observed at ∼1.9 V vs SCE. A platinum (Pt) disk (diameter: 2 mm) working electrode was used for electrochemical and ECL studies. It was polished with 0.05-μM alumina (Buehler, Lake Bluff, Illinois) on a felt pad and sonicated in absolute ethanol for 5 min. Then the electrode was heated at 70 °C for 15 min before each experiment. For the ECL measurement, acetonitrile (MeCN) solution of 0.1 mM synthesized iridium(III) complex with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte was used. In the oxidative−reductive process, 0.01 M TPA was added as a coreactant. ECL was observed using a charge-coupled device camera (LN/CCD 1752-PB/VSAR, Princeton Instruments, Trenton, NJ) cooled to below −135 °C using liquid N$_2$, and all ECL intensities were obtained with an integration time of 10 s. Solutions for ECL efficiency measurements were prepared in a drybox incorporating a N$_2$ atmosphere or were prepared in air, purged with N$_2$, and then sealed in an airtight cell. The reported values were obtained by averaging the values from at least five scans with a relative standard deviation of ∼10% in the MeCN solution.

ECL quantum efficiencies (Φ_{ECL}) during the annihilation process were calculated using a Ru(bpy)$_3^{2+}$ standard using the following equation,

$$\Phi_{ECL,Ir} = \left(\frac{I_{Ir}}{I_{Ru}}\right) \times \left(\frac{Q_{Ru}}{Q_{Ir}}\right) \times \Phi_{ECL,Ru} \qquad (1)$$

where $\Phi_{ECL,Ir}$ is the ECL quantum efficiency of synthesized (pq)$_2$Ir(LX); $\Phi_{ECL, Ru}$, the ECL quantum efficiency of the standard; I, the integrated ECL intensity; and Q, the number of total coulombs from the electrochemical generation of redox ion pairs. When the stepwise potential was applied, current response from generating (pq)$_2$Ir(LX)$^+$ and (pq)$_2$Ir(LX)$^-$ showed the same values, and the number of total coulombs was about the same with the Ru(bpy)$_3^+$/Ru(bpy)$_3^{3+}$ couple.

A cyclic voltammogram was recorded to establish the exact position of the redox processes against the AgQRE before each ECL experiment. Because of the probable drift of the potential, a cyclic voltammogram was also recorded after the ECL experiment, and no discernible drift of the AgQRE was obtained.

Chemicals. Commercially available acetylacetone (acacH, Aldrich), picolinic acid (picoH, Aldrich), 3-isoquinolinecarboxylic acid (3-iqH, Aldrich), 2,2,6,6-tetramethyl-3,5-heptanedione (tmd), and 1,3-diphenyl-1,3-propanedione (dbm) were converted to sodium salt with excess aq NaOH. 2-Phenylquinoline (pqH, TCI) and quinaldic acid sodium salt (Na(quin), TCI) were used as received without further purification. Solvents were purified as described in the literature and were purged with N$_2$ for at least 10 min prior to the experiments. Monomeric bis-(2-phenylquinolyl)Ir(III) complexes with monoanionic bidentate ligand (LX, LX = acac, tmd, dbm, pico, 3-iq, and quin) were prepared via chloride-bridged bis(2-phenylquinolyl)Ir(III) dimers as described previously.[33] NMR spectra were recorded on Bruker DPX 300-, Avance 500-, or 600-MHz instruments (Bruker Biospin, Germany) at 300 K. Elemental analyses were carried out with a CI Instrument model EA1110 and MS spectra with a Jeol JMS-AX505WA (JEOL).

Synthesis of [$C \wedge N_2$IrCl]$_2$. Cyclometalated Ir(III) μ-chloro-bridged dimers of general formula $C \wedge N_2$Ir(μ-Cl)$_2$Ir$C \wedge N_2$ were synthesized following the method reported by Nonoyama, which involves refluxing IrCl$_3$·nH$_2$O (Strem, MA) with 2−2.5 equiv

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of cyclometalating ligand in a 3:1 mixture of 2-ethoxyethanol (Aldrich) and water.[35] Concentrated HCl was added to the reaction mixture to dissolve out the remained $HC \wedge N$ ligand.

Synthesis of $\underline{C \wedge N_2}$Ir(LX) Complexes. *General Procedure.* $[\underline{C \wedge N_2}IrCl]_2$ complex (0.078 mmol), monoanionic bidentate ligand (LX, 0.2 mmol), and 0.1 mL of 2 N NaOH were stirred in 2-ethoxyethanol for 24 h. The colored precipitate was filtered off, washed with ethanol and hexane, and dissolved in dichloromethane. The crude product was purified by flash chromatography (silica/dichloromethane) or recrystallization to give the pure $\underline{C \wedge N_2}$Ir(LX) (70−90%).

(pq)₂Ir(acac). Iridium(III) bis(2-phenylquinolato-N, $C^{2'}$) acetylacetonate (yield 85%). ^{1}H NMR (500 MHz, DMSO-d_6), ppm: 8.52 (d, 2H, $J = 8.8$ Hz), 8.38 (m, 4H), 8.01 (m, 4H), 7.56 (m, 4H), 6.89 (t, 2H, $J = 7.5$ Hz), 6.54 (t, 2H, $J = 7.3$ Hz), 6.29 (d, 2H, $J = 7.6$ Hz), 4.70 (s, 1H), 1.46 (s, 6H). Anal. Found: C 59.76, H 3.86, N 3.92. Calcd: C 60.07, H 3.89, N 4.00. FAB-MS: calcd M$^+$ 700.17; observed M$^+$ 700.

(pq)₂Ir(tmd). Iridium(III) bis(2-phenylquinolato-N, C^2) (2,2′,6,6′-tetramethylhepta-3,5-dionate) (yield 85%). ^{1}H NMR (500 MHz, DMSO-d_6), ppm: 8.48 (d, 2H, $J = 8.8$ Hz), 8.38 (d, 2H, $J = 8.9$ Hz), 8.27 (d, 2H, $J = 8.6$ Hz), 8.01 (d, 2H, $J = 7.2$ Hz), 7.97 (d, 2H, $J = 7.5$ Hz), 7.53 (t, 2H, $J = 7.4$ Hz), 7.38 (t, 2H, $J = 7.9$ Hz), 6.88 (t, 2H, $J = 7.6$ Hz), 6.55 (t, 2H, $J = 7.4$ Hz), 6.37 (d, 2H, $J = 7.6$ Hz), 4.90 (s, 1H), 0.56 (s, 18H). Anal. Found: C 62.80, H 5.10, N 3.53. Calcd: C 62.81, H 5.01, N 3.57. FAB-MS: calcd M$^+$ 784.26; observed M$^+$ 784.

(pq)₂Ir(dbm). Iridium(III) bis(2-phenylquinolato-N, $C^{2'}$) (dibenzoyl methane) (yield 78%). ^{1}H NMR (500 MHz, DMSO-d_6), ppm: 8.47 (m, 6H), 8.10 (d, 2H, $J = 7.3$ Hz), 7.94 (d, 2H, $J = 8.0$ Hz), 7.53 (d, 4H, $J = 8.4$ Hz), 7.43 (t, 2H, $J = 7.4$ Hz), 7.39 (t, 2H, $J = 7.4$ Hz), 7.28 (t, 4H, $J = 7.7$ Hz), 7.18 (t, 2H, $J = 8.6$ Hz), 6.96 (t, 2H, $J = 7.4$ Hz), 6.61 (t, 2H, $J = 7.9$ Hz), 6.40 (d, 2H, $J = 7.7$ Hz), 6.01 (s, 1H). Anal. Found: C 65.94, H 3.79, N 3.35. Calcd: C 65.60, H 3.79, N 3.40. FAB-MS: calcd M$^+$ 824.20; observed M$^+$ 824.

(pq)₂Ir(pico). Iridium(III) bis(2-phenylquinolato-N, $C^{2'}$) picolinate (yield 85%). ^{1}H NMR (500 MHz, DMSO-d_6), ppm: 8.64 (d, 1H, $J = 8.6$ Hz), 8.57 (d, 1H, $J = 8.7$ Hz), 8.48 (m, 3H), 8.22 (d, 1H, $J = 7.9$ Hz), 8.06 (d, 1H, $J = 7.5$ Hz), 8.00 (d, 1H, $J = 7.2$ Hz), 7.94 (d, 1H, $J = 9.3$ Hz), 7.85 (m, 2H), 7.60 (d, 1H, $J = 7.3$ Hz), 7.56 (m, 1H), 7.50 (m, 2H), 7.41 (m, 1H), 7.22 (d, 1H, $J = 8.7$ Hz), 7.05 (t, 1H, $J = 7.9$ Hz), 6.96 (m, 2H), 6.73 (t, 1H, $J = 7.1$ Hz), 6.64 (m, 2H), 6.11 (d, 1H, $J = 7.3$ Hz). Anal. Found: C 59.49, H 3.33, N 5.78. Calcd: C 59.82, H 3.35, N 5.81. FAB-MS: calcd M$^+$ 723.15; observed M$^+$ 723.

(pq)₂Ir(quin). Iridium(III) bis(2-phenylquinolato-N, $C^{2'}$) quinaldate (yield 85%). ^{1}H NMR (300 MHz, DMSO-d_6), ppm: 8.80 (d, 1H, $J = 9.7$ Hz), 8.59 (d, 1H, $J = 8.8$ Hz), 8.48 (d, 1H, $J = 8.8$ Hz), 8.40 (d, 1H, $J = 8.5$ Hz), 8.33 (m, 2H), 8.20 (d, 1H, $J = 7.8$ Hz), 8.01 (m, 3H), 7.83 (m, 2H), 7.70 (d, 2H, $J = 8.9$ Hz), 7.57 (d, 1H, $J = 15.8$ Hz), 7.44 (m, 2H), 7.32 (m, 2H), 7.06 (t, 1H, $J = 25.7$ Hz), 6.96 (t, 1H, $J = 15.0$ Hz), 6.76 (t, 1H, $J = 14.5$ Hz), 6.65 (m, 3H), 6.00 (d, 1H, $J = 7.7$ Hz). Anal. Found: C 62.03, H 3.39, N 5.33. Calcd: C 62.16, H 3.39, N 5.44. HR-FAB-MS: calcd M$^+$ 773.17; observed M$^+$ 773.2876.

(pq)₂Ir(3-iq). Iridium(III) bis(2-phenylquinolato-N, $C^{2'}$) (3-isoquinaldate) (yield 85%). ^{1}H NMR (300 MHz, DMSO-d_6), ppm: 8.70 (m, 1H), 8.48 (m, 5H), 8.27 (d, 1H, $J = 7.3$ Hz), 8.16 (s, 1H), 8.02 (m, 4H), 7.84 (m, 2H), 7.72 (t, 1H, $J = 8.2$ Hz), 7.47 (m, 2H), 7.41 (d, 1H, $J = 8.7$ Hz), 7.31 (t, 1H, $J = 7.6$ Hz), 7.12 (t, 1H, $J = 8.0$ Hz), 6.97 (t, 1H, $J = 7.9$ Hz),
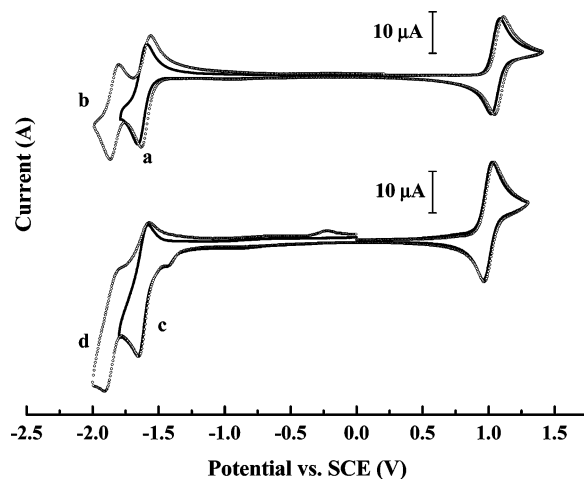
Figure 2. Cyclic voltammograms of 1 mM (pq)₂Ir(pico): (a) scan to −1.8 V, (b) scan to −2.0 V and 1 mM (pq)₂Ir(acac), (c) scan to −1.8 V, and (d) scan to −2.0 V in the MeCN solution. The scan rate is 0.2 V/s, and the supporting electrolyte is 0.1 M TBAPF₆.

6.77 (m, 2H), 6.65 (m, 2H), 6.13 (d, 1H, $J = 9.2$ Hz). HR-FAB-MS: calcd M$^+$ 789.19; observed M$^+$ 789.1932.

Results and Discussion

Synthesis and Structural Property of (pq)₂Ir(LX) Complexes. High-ECL-producing cyclometalated Ir(III) complexes were prepared by cleaving (pq)₂Ir(−Cl−)₂Ir(pq)₂ with excess *LX*H ligand under the base condition. All the iridium(III) complexes in the present study exhibited similar UV (not shown here) and PL in dichloromethane. On the basis of the similarity of the spectra and the inclusion of a heavy metal ion in the center of the metal complex, the emission from (pq)₂Ir(LX) was assumed to be ³MLCT with (pq)₂Ir moiety, following the assignment of the emission state for (pq)₂Ir(acac) reported in the literature.[33]

Electrochemistry. CV was employed to study the electrochemical properties of these complexes, in which the $i-V$ response can provide information on the kinetics of the electron-transfer reaction and thermodynamics of the electrode−electrolyte interface. Figure 2a shows a representative cyclic voltammogram of the (pq)₂Ir(LX) complexes, (pq)₂Ir(pico), at the Pt disk working electrode in MeCN solution with 0.1 M TBAPF₆ as the supporting electrolyte. The observed waves were assigned to (pq)₂Ir(pico)$^{0/+1}$ for the oxidative process and to (pq)₂Ir(pico)$^{0/-1}$ and (pq)₂Ir(pico)$^{-1/-2}$ for the reductive processes. The standard oxidation potential (E^0_{ox}) for (pq)₂Ir(pico)$^{0/+1}$ was 1.04 V, and the reduction potential (E^0_{red}) for (pq)₂Ir(pico)$^{0/-1}$ was −1.62 V vs SCE. Redox chemistry showed that the peak current ratio (i_{pc}/i_{pa}) and peak separation (ΔE_{pp}) for the (pq)₂Ir(pico)$^{0/+1}$ pair were 0.90 and 69 mV, whereas those for the (pq)₂Ir(pico)$^{0/-1}$ pair were 0.96 and 69 mV, respectively, at 0.2 V/s (Table 1); this indicated a reversible one-electron-transfer system. The other iridium complexes also exhibited reversible or quasireversible oxidation and reduction waves at a scan rate of 0.2 V/s. The redox behavior of the iridium complexes showed $i_{pc}/i_{pa} = \sim 0.86-0.98$ for the (pq)₂Ir(LX)$^{0/+1}$ pair and $i_{pa}/i_{pc} = \sim 0.91-0.98$ for the (pq)₂Ir(LX)$^{0/-1}$ pair, indicating a quasireversible oxidation and reduction system (Table 1). The values of ΔE_{pp} for the (pq)₂Ir(LX)$^{0/+1}$ and (pq)₂Ir(LX)$^{0/-1}$ pairs at 0.2 V/s were $\sim 65-85$ and $\sim 69-77$ mV, respectively; these values also indicated one-electron processes. Furthermore, (pq)₂Ir(acac), which showed irreversible reduction waves, had $i_{pa}/i_{pc} = 0.37$ for the (pq)₂Ir(acac)$^{0/-1}$ pair (Figure 2c). This implies that the

ECL of Bis-Cyclometalated (pq)2Ir(LX) Complexes

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TABLE 1: Electrochemical Data of $(pq)_2Ir(LX)$ Complexes[a]

complexes	oxidative process			reductive process		
	E_{ox}^0, V	i_{pc}/i_{pa}	ΔE_{pp}, V	E_{red}^0, V	i_{pa}/i_{pc}	ΔE_{pp}, V
$(pq)_2Ir(quin)$	1.16	0.72	0.085	−1.45	0.94	0.077
$(pq)_2Ir(3\text{-}iq)$	1.19	0.92	0.065	−1.48	0.92	0.076
$(pq)_2Ir(pico)$	1.04	0.90	0.069	−1.62	0.96	0.069
$(pq)_2Ir(acac)$	0.99	0.86	0.065	−1.63	0.37	0.076
$(pq)_2Ir(tmd)$	0.91	0.95	0.065	−1.72	0.98	0.070
$(pq)_2Ir(dbm)$	1.08	0.98	0.070	−1.53	0.91	0.077

[a] All electrochemical data were determined at room temperature in MeCN solution containing 0.1 M TBAPF$_6$. All potentials were referenced to SCE.
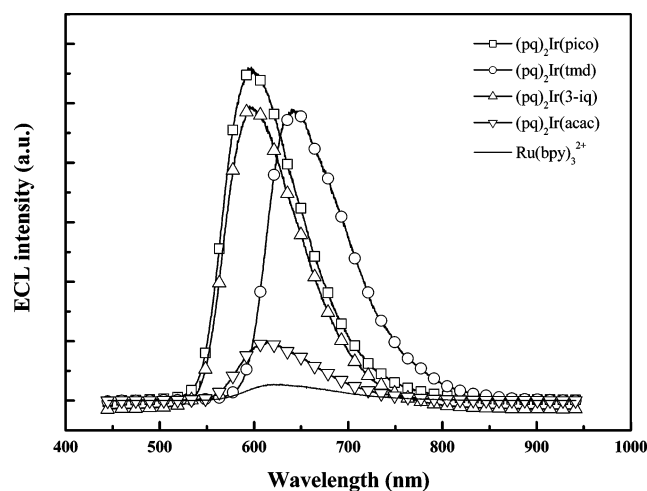

Figure 3. Annihilation ECL spectra of $(pq)_2Ir(LX)^+/(pq)_2Ir(LX)^-$ systems; 0.1 mM Ir(III) complexes are present in MeCN solution containing 0.1 M TBAPF$_6$ as the supporting electrolyte.

TABLE 2: Spectroscopic and ECL Data for Iridium Complexes

complexes	ΔG $(-\Delta E^0)$ eV	E_T eV	λ_{PL} nm	Φ_{PL}	I/I_{Ru}[a] annihilation $(\Phi_{ECL}$[b]$)$	with TPA	with $S_2O_8^{2-}$
$(pq)_2Ir(quin)$	−2.61	2.17	571	0.28	0.69 (0.03)	18	18
$(pq)_2Ir(pico)$	−2.66	2.17	571	0.27	18 (0.88)	26	25
$(pq)_2Ir(3\text{-}iq)$	−2.67	2.17	572	0.18	12 (0.61)	38	8.6
$(pq)_2Ir(acac)$	−2.62	2.10	589	0.10	3.1 (0.16)	77[c]	5.2
$(pq)_2Ir(tmd)$	−2.63	2.10	590	0.10	16 (0.80)	48[c]	26
$(pq)_2Ir(dbm)$	−2.61	2.09	588	0.03	0.46 (0.02)	6.5	0.21
$Ru(bpy)_3^{2+}$	−2.61	2.04	608	0.05	1.0 (0.05[b])	1.0	1.0

[a] The ratio of the integrated ECL intensity of the $(pq)_2Ir(LX)/$ coreactant system (I/I_{Ru}) was referenced to $Ru(bpy)_3^{2+}/$coreactant as the standard (I_{Ru}). [b] Φ_{ECL} were calculated with respect to the ECL efficiency of $Ru(bpy)_3^{2+}$ of $\Phi_{ECL,Ru} = \sim 0.05$ in MeCN.[21] Reported values were averaged from at least five scans with a relative standard deviation of $\sim 10\%$ in MeCN solutions. [c] See reference 31.

The generation of excited $(pq)_2Ir^*(LX)$ by pulsing the potential can be similarly explained on the basis of the extensively studied $Ru(bpy)_3^{2+}$ system via the following mechanistic processes:[6]

$$(pq)_2Ir(LX)^{\bullet+} + (pq)_2Ir(LX)^{\bullet-} \rightarrow (pq)_2Ir^*(LX) + (pq)_2Ir(LX) \quad (2)$$
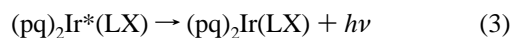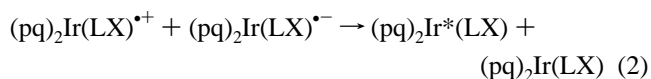
$$(pq)_2Ir^*(LX) \rightarrow (pq)_2Ir(LX) + h\nu \quad (3)$$

In annihilation ECL, the electron-transfer reaction between $(pq)_2Ir(LX)^{\bullet+}$ and $(pq)_2Ir(LX)^{\bullet-}$ is the dominant channel for the generation of excited $(pq)_2Ir^*(LX)$. This exergonic electron-transfer reaction with a sufficient energy (ΔG of ca. −2.67 to −2.61 eV) can populate the excited $(pq)_2Ir^*(LX)$ with an energy, E_T, of $\sim 2.17-2.09$ eV (Table 2).[1,3,39] Therefore, it is possible that most of the $(pq)_2Ir(LX)$s produce efficient emission in the annihilation process (Figure 3). To obtain a more quantitative measurement of the ECL efficiency, the integration of the emission curve is mainly used in the conventional method (Table 2).[23] The ratio of the integrated ECL intensity from the $(pq)_2Ir(LX)^{\bullet+}/(pq)_2Ir(LX)^{\bullet-}$ couple is $I/I_{Ru} = \sim 0.46-18$, which is compared to that of the $Ru(bpy)_3^{1+}/Ru(bpy)_3^{3+}$ system ($= I_{Ru}$). These values correspond to the ECL efficiencies of $\Phi_{ECL} = \sim 0.02-0.88$, where the ECL efficiency of the $Ru(bpy)_3^{1+}/Ru(bpy)_3^{3+}$ couple is $\Phi_{ECL} = \sim 0.05$ under similar conditions (eq 1).[21]

The ECL efficiency is defined as the ratio of the number of photons emitted to the consumed charge for producing annihilation ECL. Since the charge passed for each complex is approximately the same as that passed for the $Ru(bpy)_3^{1+}/Ru(bpy)_3^{3+}$ couple under the given conditions, the ECL efficiencies could be easily estimated by comparing the integrated emission intensity with that of $Ru(bpy)_3^{2+}$.

The ECL efficiency is often expressed as the combination of the yield of the excited-state generation (Φ_{ES}) and the PL QY (Φ_{PL}) of a luminescent material;[39] therefore, from a conventional view point, it is impossible that the value of ECL efficiency is higher than that of PL QY. This can be correctly applied to a fluorescent dye in which the emission is produced only from the excited singlet states. As shown in Table 2, however, the annihilation process from some of the $(pq)_2Ir(LX)$ complexes exhibits a highly efficient ECL whose efficiencies far exceed its PL QY. Furthermore, to the best of our knowledge, $\Phi_{ECL} = 0.88$ in the case of $(pq)_2Ir(pico)$ is the highest value reported thus far. In addition, in Table 2, the ECL efficiencies of the complexes show discordant tendencies with their respective PL

electrochemically produced $(pq)_2Ir(acac)^{\bullet-}$ anion radicals are unstable to some extent at the given scan rate. The reduction also showed irreversible behavior at scan rates faster than 2 V/s. $(pq)_2Ir(quin)$ ($i_{pc}/i_{pa} = 0.72$ and $\Delta E_{pp} = 85$ mV for the $(pq)_2Ir(quin)^{0/+1}$ pair) exhibited a less reversible character during the oxidative process, in contrast to its reversible reductive waves. Although the peak current and peak separation for the $(pq)_2Ir(quin)^{0/-1}$ pair suggests a one-electron process, $i_{pc}/i_{pa} = 0.72$ for the $(pq)_2Ir(quin)^{0/+1}$ pair implies that less stable $(pq)_2Ir(quin)^{\bullet+}$ cation radicals are formed in the MeCN solution.

In all $(pq)_2Ir(LX)$ complexes, oxidation is considered to be a metal−aryl-centered process, whereas reduction is mainly localized on the pyridyl rings of the cyclometalating ligands.[36-38] Therefore, it is considered that the single one-electron oxidation of $(pq)_2Ir(LX)$ occurs at the $(pq)_2Ir$-based HOMO and each pyridyl ring of the (pq) ligands allows two one-electron reductions.

Annihilation ECL Process. Efficient ECL from the synthesized iridium(III) complexes was observed by pulsing the potential of the Pt working electrode between the oxidation and reduction potentials of the complexes (Figure 3). For solutions containing 0.1 mM $(pq)_2Ir(LX)$ and 0.1 M TBAPF$_6$ as the supporting electrolyte, intense ECL emission visible even under daylight was produced. The ECL spectra are similar to the PL spectra; therefore, the same ^{3}MLCT states are probably formed during both experiments. The emission spectra of the complexes are centered around 600 nm and shift slightly to longer wavelengths, as compared to their PL, because of the increase of concentration.

QYs. This implies that the ECL efficiency cannot be simply estimated directly from the PL QY, which makes it necessary to consider other factors, as well.

In photoluminescence (PL) processes, the optically induced (or photochemical) excitation can populate electrons in the singlet S_1 state; thereafter, they decay radiatively (with a decay rate $k_{R(S)}$) or nonradiatively (with a decay rate $k_{NR(S)}$) to the singlet ground S_0 state or undergo intersystem crossing (ISC) to the triplet manifold (with a rate k_{ISC}). Both radiative and nonradiative decays also occur from the triplet T_1 state to the ground S_0 state (with decay rates of $k_{R(T)}$ and $k_{NR(T)}$). The excitation processes in ECL are very similar to those in PL; however, an important difference is that the triplet excitation can be created directly in ECL. Therefore, the probabilities of generating singlet excitation (χ_S) and triplet excitation (χ_T) in the electrogeneration process are very critical to the total PL QYs, including both fluorescence and phosphorescence. Annihilation ECL processes are very similar to solid-state electroluminescence (EL) processes in which holes and electrons are produced in multilayer thin films and recombined with each other under the applied electric field.[40] It has recently been reported that in EL processes, electrochemically induced excitation can populate the triplet and singlet states simultaneously; therefore, EL efficiency with higher values than the PL QY can be interpreted by the contribution of direct triplet excitation.[41,42] A similar explanation can be applied to the higher ECL efficiency of $(pq)_2Ir(LX)$s than the PL QY, in which almost all the luminescence is coming from the triplet excited state.

The discordant tendency of ECL efficiencies with PL QYs can also be attributed to the electrochemical stability of radical ions. From a qualitative viewpoint, ECL is a result of a series of chemical reactions between electrochemically produced radical ions, and the electrochemical stability of the radical ions significantly affects the population of the excited states for efficient ECL process.

On the basis of the similarity of electron−hole recombinations, we can express the ECL efficiency in terms of the electrochemical stability of radical ions and electrochemical excitation with reference to the recent reports of Adachi et al. on EL processes.[43,44] Since direct excitation to the singlet S_1 state is allowed only in optical excitation and only phosphorescence is possible in $(pq)_2Ir(LX)$ complexes, the phosphorescence quantum yield is the same as PL QY (Φ_{PL}) and expressed in terms of intersystem crossing from the metal-to-ligand charge-transfer singlet S_1,

$$\Phi_{PL} = \Phi_{ISC} \times \left(\frac{k_R}{k_R + k_{NR}}\right) \quad (4)$$

where Φ_{ISC} represents the probability of ISC. In electrochemical excitation, both the singlet S_1 and the triplet T_1 can populate simultaneously,[6,22] which can be a trigger of higher ECL efficiency than PL QY. By considering the electrochemical stability of radical ions, the ECL efficiency can be expressed as follows,

$$\Phi_{ECL} = \Phi_{ES} \times \left[\chi_T\left(\frac{k_R}{k_R + k_{NR}}\right) + \chi_S\Phi_{ISC}\left(\frac{k_R}{k_R + k_{NR}}\right)\right] \quad (5)$$

where Φ_{ES} is the excitation quantum yield resulting from the electrochemical stability of radical ions and subsequent recombination. Due to the statistical splitting of $\chi_S \sim 25\%$ and $\chi_T \sim$

75% and the fact that $\chi_S + \chi_T = 1$,[45] eq 5 becomes

$$\Phi_{ECL} \approx \Phi_{ES} \times [0.75 + 0.25 \times \Phi_{ISC}]\,[k_R/(k_R + k_{NR})] \quad (5a)$$

If the intrinsic phosphorescence efficiency approaches the maximum value (i.e., $[k_R/(k_R + k_{NR})] = 1$), as noted by Adachi et al.,[43] in the case of $(pq)_2Ir(pico)$, Φ_{ISC} can be estimated to be 0.27 from the PL QY (i.e., from $\Phi_{PL} = 0.27$) in eq 4. Because $(pq)_2Ir(pico)$ exhibits electrochemically stable redox behavior in both the oxidative and reductive processes at 0.2 V/s, Φ_{ES} is assumed to be almost unity during the 10-Hz pulsing. Consequently, from eq 5a, the ECL efficiency can be roughly calculated as $\Phi_{ECL} = 0.82$, which is reasonably close to the measured value of 0.88.

Inefficient ECL from $(pq)_2Ir(acac)$ or $(pq)_2Ir(quin)$, which showed a high PL QY, can be understood primarily in terms of the electrochemical stability. For $(pq)_2Ir(acac)$, electrochemically unstable $(pq)_2Ir(acac)^{\bullet-}$ anion radicals induce irreversible electrochemical behavior in the reductive process and, consequently, cause less intense emission in annihilation ECL. Figure 2c shows the irreversible reduction waves of $(pq)_2Ir(acac)$ in the reductive process. When the potential is swept to −2.0 V, a second irreversible reduction peak is observed. Moreover, small oxidation peaks that are visible after scan reversal following the reduction peak between −0.1 and −0.3 V vs SCE are attributed to decomposition products formed upon the reduction of the compounds (Figure 2d). The instability of $(pq)_2Ir(acac)^{\bullet-}$ anion radicals can be seen from the peak current ratio of $(pq)_2Ir(acac)^{0/-1}$, which is only 0.36 (Table 1). In the case of $(pq)_2Ir(quin)$, less reversible oxidation appeared to be one of the major factors responsible for constraining efficient emission.

The effect of the unstable anion radicals also contributes to the reductive−oxidative process of the $(pq)_2Ir(LX)/S_2O_8^{2-}$ couples. In the reductive−oxidative process, the strong oxidant $SO_4^{\bullet-}$, which is produced from $S_2O_8^{2-}$, oxidizes $(pq)_2Ir(LX)^{\bullet-}$ to populate the excited $(pq)_2Ir^*(LX)$. The more stable the anion radicals ($(pq)_2Ir(LX)^{\bullet-}$), the more intense ECL that can be produced from the reaction with $SO_4^{\bullet-}$. In the presence of excess $S_2O_8^{2-}$ (10 mM), all $(pq)_2Ir(LX)$s produce intense ECL by reacting with $SO_4^{\bullet-}$ in the reductive−oxidative process (Table 2). In Table 2, the complexes (e.g., $(pq)_2Ir(tmd)$ and $(pq)_2Ir(3-iq)$) that show reversible redox behavior in both the reductive and oxidative processes produce efficient ECL in both the reductive−oxidative and annihilation processes. In contrast, $(pq)_2Ir(acac)$, which shows irreversible reduction waves, generates less intense emission in both the reductive−oxidative and annihilation processes.
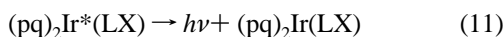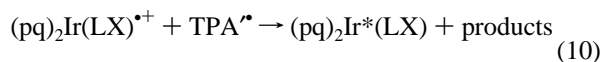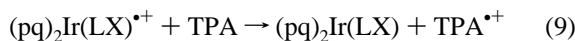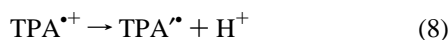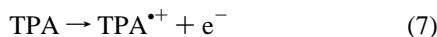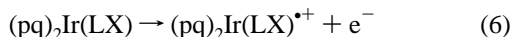
Figure 4 shows the correlation between annihilation ECL and reductive−oxidative ECL. $(pq)_2Ir(quin)$, which deviates from the others and produces efficient ECL with $S_2O_8^{2-}$ but less intense annihilation ECL, perhaps due to the irreversible nature of the oxidation reaction. The electrochemical redox stability of luminophores is, thus, believed to be one of the main factors that determine the ECL intensity. The emission intensities of all of the complexes decrease over time, presumably because of the decomposition of the redox products during the electrochemical process. Among the $(pq)_2Ir(LX)$ complexes, the decrease in emission is the quickest in the case of $(pq)_2Ir(acac)$. This also supports our conclusion that the transient lifetime of the $(pq)_2Ir(LX)^{\bullet-}$ anion radicals is important for the production of light in annihilation ECL.

Oxidative−Reductive Process. We have already reported the origin of ECL on the basis of the energetics of the

ECL of Bis-Cyclometalated (pq)2Ir(LX) Complexes

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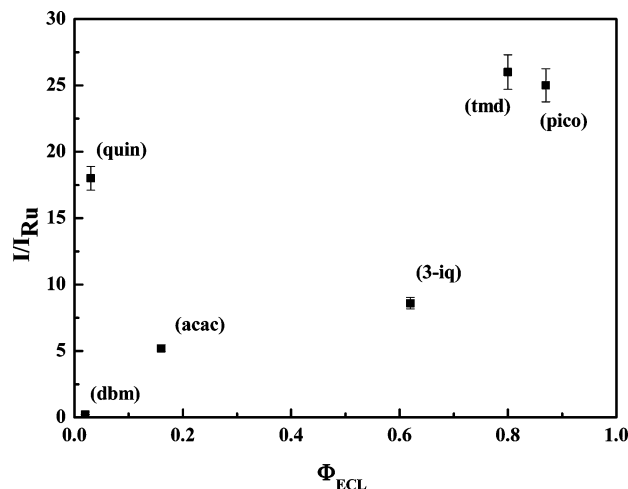
Figure 4. Correlation diagram between relative ECL intensity (I/I_{Ru}) by reductive−oxidative process and ECL efficiency (Φ_{ECL}) by annihilation process. I/I_{Ru} is the ratio of integrated ECL intensities of the $(pq)_2Ir(LX)/S_2O_8^{2-}$ couple referenced to $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ as a unit value.

Figure 5. ECL spectra of $(pq)_2Ir(LX)/TPA$ systems; 0.1 mM luminophores and 10 mM TPA are present in MeCN solution containing 0.1 M TBAPF$_6$ as the supporting electrolyte.

luminophore/TPA system.[31] On the basis of the electrochemical and ECL experiments of $Ru(bpy)_3^{2+}/TPA$[7] and other transition metal/TPA systems,[1−4] the ECL from $(pq)_2Ir(LX)$ in the presence of TPA can be expressed by the following reactions:[31]

$$(pq)_2Ir(LX) \rightarrow (pq)_2Ir(LX)^{\bullet+} + e^- \qquad (6)$$

$$TPA \rightarrow TPA^{\bullet+} + e^- \qquad (7)$$

$$TPA^{\bullet+} \rightarrow TPA^{\prime\bullet} + H^+ \qquad (8)$$

$$(pq)_2Ir(LX)^{\bullet+} + TPA \rightarrow (pq)_2Ir(LX) + TPA^{\bullet+} \qquad (9)$$

$$(pq)_2Ir(LX)^{\bullet+} + TPA^{\prime\bullet} \rightarrow (pq)_2Ir^*(LX) + products \qquad (10)$$

$$(pq)_2Ir^*(LX) \rightarrow h\nu + (pq)_2Ir(LX) \qquad (11)$$

In the $(pq)_2Ir(LX)/TPA$ system, the generation of cation radical species $TPA^{\bullet+}$ (eqs 7 and 9) and the electrochemical reduction of $(pq)_2Ir(LX)^{\bullet+}$ cation radicals (eq 10) play key roles in light generation. Because $TPA^{\bullet+}$ cation radicals, being intermediate for $TPA^{\bullet}$ radicals generation, can be produced directly by electrochemical oxidation of TPA (eq 7), even though it is kinetically sluggish,[46,47] or indirectly by means of electrocatalytic oxidation of TPA (eq 9) on a Pt electrode in MeCN solution, the electron-transfer reaction between $(pq)_2Ir(LX)^{\bullet+}$ and $TPA^{\prime\bullet}$ can be an important factor in the ECL emission process.[31] In this report, the observation of $(pq)_2Ir(LX)$ complexes on the basis of their electrochemical behavior reveals that the reduction potentials are less negative than −1.7 V (= $E^0_{TPA^{\prime\bullet}}$, that is, the reducing power of the $TPA^{\prime\bullet}$ radical vs SCE),[48] which is sufficient to receive electrons from $TPA^{\prime\bullet}$ radicals to populate the excited state $(pq)_2Ir^*(LX)$. Therefore, the $(pq)_2Ir(LX)$ complexes are readily reduced by the electrogenerated $TPA^{\prime\bullet}$ radicals and generate excited $(pq)_2Ir^*(LX)$ in the oxidative−reductive process. Figure 5 shows the ECL generated from iridium complexes through the oxidative−reductive process with TPA. In comparison with the ECL intensities of the $Ru(bpy)_3^{2+}/TPA$ system considered as unity, the relative ECL intensities from the $(pq)_2Ir(LX)/TPA$ systems are $I/I_{Ru} = \sim 6.5-77$ (Table 2). It is interesting that all $(pq)_2Ir(LX)$ complexes employed in this study show a higher ECL
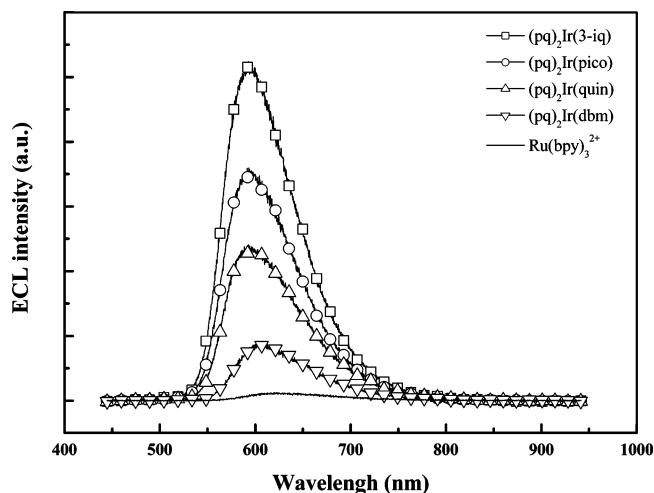
with TPA than that with $Ru(bpy)_3^{2+}$. Furthermore, $(pq)_2Ir(dbm)$ with a very low PL QY ($\Phi_{PL} = 0.03$) shows $I/I_{Ru} = 6.5$. Highly intense ECL from the $(pq)_2Ir(LX)$ complexes by the oxidative−reductive process has already been observed in our previous study.[31]

Despite the fact that the ECL intensity is related to the PL QY, no correlation can be found between them in the oxidative−reductive process. This is perhaps due to the fact that there are many competitive pathways involving both heterogeneous and homogeneous reactions in the oxidative−reductive process. The electrochemical generation of radical precursors occurs relatively easily in the annihilation process, whereas in oxidative−reductive ECL, this process is rather complicated. This is because (i) the produced $(pq)_2Ir(LX)^{\bullet+}$ cation radicals induce the electrocatalytic oxidation of TPA; (ii) then they are reduced; and (iii) finally, the produced $TPA^{\prime\bullet}$ radicals can reduce the $(pq)_2Ir(LX)^{\bullet+}$ cation radicals and $(pq)_2Ir(LX)$ molecules simultaneously. The kinetic behavior between $(pq)_2Ir(LX)^{\bullet+}$ and $TPA^{\prime\bullet}$ also differs significantly according to the substituted ligand group(s), and it influences light generation. Therefore, more complicated characteristics with respect to their PL QY would be obtained by oxidative−reductive ECL. This is similar to the case in which it is difficult to estimate the ECL behavior by annihilation directly from the PL QY. Recently, a few studies have focused on the $Ru(bpy)_3^{2+}/TPA$ system and determined its thermodynamic and kinetic parameters.[48,49] Zhou et al. have reported a similar conclusion that there is no obvious relationship between the PL QY and ECL intensity with the $Ru(bpy)_3^{2+}$ derivatives.[50] It is necessary to consider both thermodynamic and kinetic parameters in the $(pq)_2Ir(LX)/TPA$ system to gain a clear understanding of the ECL process. More studies of the behavior of ECL from iridium complexes and the role of substituted ligand(s) are required.

Conclusions

Extremely efficient ECL from bis-cyclometalated iridium-(III) complexes is obtained. The electrochemical and spectroscopic behavior of synthesized $(pq)_2Ir(LX)$ complexes are similar to those of $Ru(bpy)_3^{2+}$. Excited $(pq)_2Ir^*(LX)$s with energy E_T of $\sim 2.09-2.17$ eV are easily electrogenerated through oxidative−reductive (with TPA) and annihilation processes. Electron transfer between the $(pq)_2Ir(LX)^{\bullet+}/(pq)_2Ir(LX)^{\bullet-}$ couple is sufficiently exergonic to populate the excited $(pq)_2Ir^*(LX)$ in the annihilation process. The synthesized $(pq)_2Ir(LX)$s

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produce efficient ECL by the annihilation process, in which the ECL efficiency of $(pq)_2Ir(pico)$ reaches close to unity (i.e., Φ_{ECL} from $(pq)_2Ir(pico) = 0.88$), and ECL efficiencies often show higher values than their PL QYs. Because electrochemical excitation can populate a greater percentage of the emissive triplet state either by direct triplet excited-state generation or by intersystem crossing from singlet excited state, in comparison with optical excitation, it is possible to achieve a higher ECL efficiency with respect to PL QY. The electrochemical stability of $(pq)_2Ir(LX)^{\bullet+/\bullet-}$ radical ions also significantly affects the ECL efficiency. The PL QY is still a major factor responsible for producing efficient ECL, and therefore, $(pq)_2Ir(dbm)$ with only $\Phi_{PL} = 0.03$ shows less intense ECL. Furthermore, most of the $(pq)_2Ir(LX)$s with a high PL QY show efficient ECL. $(pq)_2Ir$-(acac) shows a high PL QY but yields irreversible reduction waves and generates a less intense ECL by the annihilation process. The influence of the electrochemical stability of $(pq)_2Ir$-(LX) is confirmed in the reductive−oxidative process. Because the ECL generation from $(pq)_2Ir(LX)/TPA$ is based on the complicated heterogeneous electrode reaction and homogeneous electron transfer, oxidative−reductive ECL exhibits a very different tendency toward the PL QY. Nevertheless, all $(pq)_2Ir$-(LX)/coreactant systems generate a more intense ECL than that from the $Ru(bpy)_3^{2+}$ system. PL QY is only one of the preliminary requisites to yield high ECL; however, the ECL intensity cannot be predicted directly from PL QY. To the best of our knowledge, the efficient ECL from $(pq)_2Ir(LX)$ complexes (up to $\Phi_{ECL^-} = 0.88$) has the highest efficiency ever reported, and ECL from bis-cyclometalated iridium(III) complexes, which have (pq) moieties, requires further studies. These results are useful for future studies on analytical applications and provide information for developing efficient electroluminescent devices.

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