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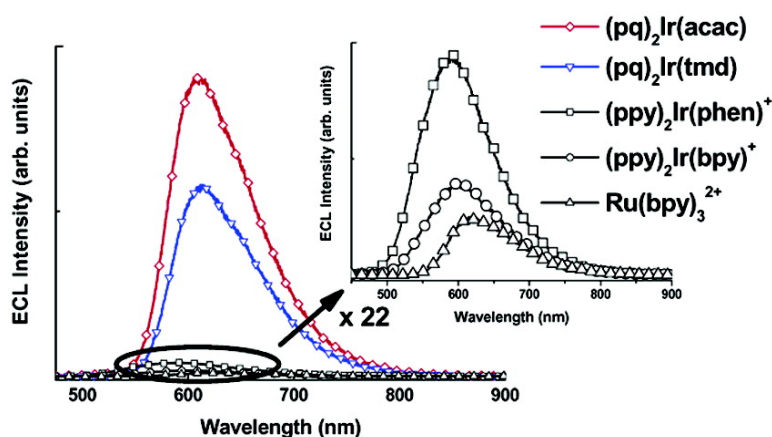
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Efficient Electrogenerated Chemiluminescence from Cyclometalated Iridium(III) Complexes

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Electrogenerated chemiluminescence (ECL) is a well-known method for generating light; electrochemically generated radical ions undergo a homogeneous electron transfer to produce the excited state that releases the excited energy as light.[1] ECL has long been of interest because it provides a simple light production mechanism for various applications and some insight into the light-emitting mechanisms.[2c] Among the various materials investigated for ECL study, an important branch is metal complexes due to their thermal and photochemical stability and high photoluminescence (PL) efficiency, and most of the ECL studies on metal complexes have focused on tris(2,2′-bipyridine)ruthenium(II) (Ru(bpy)$_3^{2+}$). ECL of Ru(bpy)$_3^{2+}$ has also attracted much attention as a sensitive and selective detection method in analytical chemistry.[2a,b,d] Recently, organometallic materials used in OLED (organic light emitting devices) such as Alq$_3$[3a] and cyclometalated Ir(III) complexes[3c−f] have been studied as new ECL reagents. Since these materials have high PL efficiencies compared to the low PL efficiency of Ru(bpy)$_3^{2+}$ ($\Phi_{PL} = 0.042$), some ECL studies on annihilations of self-radical and cross-radical ions have been carried out.[3c−e] Although self-radical annihilation ECL of *fac*-Ir(ppy)$_3$, one of the highly efficient OLED materials, showed very high ECL efficiency comparable to its PL efficiency ($\Phi_{PL} = 0.4$),[3c,e] Richter et al. have reported that ECL studies of *fac*-Ir(ppy)$_3$ with tri-*n*-propylamine (TPA) gave a low ECL (about one-third of the value for Ru(bpy)$_3^{2+}$/TPA).[3d] This unexpected result forced us to investigate the origin of the low ECL on the basis of the energetics of the *fac*-Ir(ppy)$_3$/TPA system.

When an excess amount of TPA is employed as a co-reactant, an emitter complex (E) is reversibly oxidized to E$^{+\bullet}$ at an electrode and then interacts with TPA$^\bullet$, which is irreversibly generated by oxidation and decomposition of TPA at the electrode, to receive an electron and form an excited-state species, E*, as shown in the following reaction sequences:[4]

$$E - e^- \rightarrow E^{+\bullet} \tag{1}$$

$$TPA - e^- \rightarrow TPA^{+\bullet} \tag{2}$$

$$E^{+\bullet} + TPA \rightarrow E + TPA^{+\bullet} \tag{2'}$$

$$TPA^{+\bullet} \rightarrow TPA^\bullet + H^+ \tag{3}$$

$$E^{+\bullet} + TPA^\bullet \rightarrow E^* + TPA' \text{ (side product)} \tag{4}$$

It is known that these species could also be generated by other electron-transfer reactions, represented as

$$E + TPA^\bullet \rightarrow E^{-\bullet} + TPA' \text{ (side product)} \tag{5}$$

$$E^{+\bullet} + E^{-\bullet} \rightarrow E^* + E \tag{6}$$

To realize high ECL efficiency, the electron-transfer reactions in reactions 2′, 4, and 6 should occur effectively since direct oxidation of TPA on a Pt electrode (reaction 2) usually occurs

relatively slowly in a positive applied potential ($\sim$0.90 V vs SCE), and oxidation of the emitter (reaction 1) could occur relatively fast.[3b] A self-radical ion annihilation experiment with *fac*-Ir(ppy)$_3$ related to reaction 6 is known to give high ECL intensity.[3c,e] Therefore, for the effective formation of excited-state E* in this ECL system, (i) the oxidation potential of the emitter ($\epsilon°(E^{+\bullet}/E)$) should be positive enough for an efficient generation of TPA$^+$ and (ii) the potential of the TPA$^\bullet$ donor should be more negative than the reduction potential of E ($\epsilon°(E/E^{-\bullet})$ or $\epsilon°(E^{+\bullet}/E)$, $\sim$LUMO energy level of E as shown in Scheme 1.

**Scheme 1.** Postulated Efficient ECL Route[a]
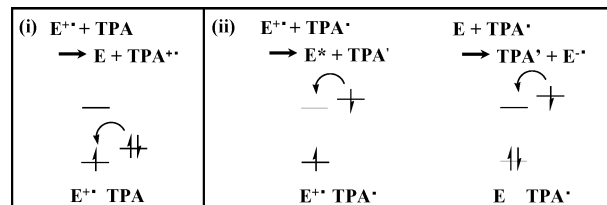
[a] (i) The high oxidation potential ensures the efficient generation of TPA radicals by generating an emitter cation radical (E$^{+\bullet}$) which in turn removes an electron from a HOMO level of TPA. (ii) The acceptor energy level (LUMO of E) should be lower than the potential of the TPA$^\bullet$ donor energy level.

Bard's group recently reported on excellent work to determine the reducing power of TPA$^\bullet$, a strong reductant radical formed from irreversible oxidation of TPA, in solution by ECL quenching experiments ($\epsilon°(TPA^\bullet) = \sim -1.7$ V).[5] We have attempted to deal with the low ECL efficiency for high PL materials by deliberately selecting materials having a reduction potential lower than the experimental reducing power of TPA and having a more positive oxidation potential than the reference oxidation potential of *fac*-Ir(ppy)$_3$ to induce fast generation of TPA$^\bullet$ via an emitter cationic radical.

Several cationic and neutral tris-chelate iridium(III) complexes, [ppy$_2$Ir(bpy)]$^+$, [ppy$_2$Ir(phen)]$^+$, (pq)$_2$Ir(acac), and (pq)$_2$Ir(tmd) (ppy = 2-phenylpyridine anion, pq = 2-phenylquinoline anion, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, acac = acetylacetonate anion, and tmd = 2,2′,6,6′-tetramethylhepta-3,5-dione anion),[6b−d] satisfying our postulation, were prepared by cleaving chloride-bridged Ir(III) complexes with an excess amount of appropriate ligand (bpy, phen, acac, or tmd; Figure 1). All these complexes are highly soluble in common polar solvents for ECL experiments, such as DMSO, DMF, 1,4-dioxane, and MeCN; PF$_6^-$ salt forms were used for cationic complexes.

The optical and electrochemical properties are summarized in Table 1. The origin of absorption and emission of the complexes has been assigned as the triplet metal-to-ligand charge-transfer (MLCT) transitions following the literature convention.[6,7b] Strong spin−orbit coupling of central metal atoms facilitates the spin-forbidden ^{3}MLCT transitions of the metal complexes. This intense
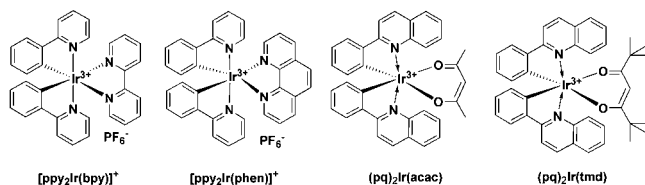
Figure 1. Metal complexes used in ECL study: $[ppy_2Ir(bpy)]^+$, $[ppy_2Ir(phen)]^+$, $(pq)_2Ir(acac)$, and $(pq)_2Ir(tmd)$.

Table 1. Optical and Electrochemical Properties of Metal Complexes

complex	photoluminescence		electrochemistry (V vs SCE)			
	λ_{max}/ nm	$\Phi_{PL}{}^a$	$\epsilon°(ox)^b$	$\epsilon°(red)^b$	λ_{max}/ nm^c	rel Φ_{ECL}
$Ru(bpy)_3{}^{2+}$	608	0.042	1.35	−1.33	618	1^d
fac-$Ir(ppy)_3$	510	0.40	0.86	−2.2	517	0.33^e
$[(ppy)_2Ir(bpy)]^+$	606	0.06	1.15	−1.51	606	2^d
$[(ppy)_2Ir(phen)]^+$	599	0.14	1.15	−1.47	606	4^d
$(pq)_2Ir(acac)$	589	0.10	0.99	−1.63	609	77^f
$(pq)_2Ir(tmd)$	593	0.10	0.91	−1.72	615	49^f

^{a} Values obtained in thoroughly degassed dichloromethane solution using Rhodamine 6G in ethanol (Φ_{PL}=0.95) as a standard. ^{b} Values obtained in acetonitrile. ^{c} ECL λ_{max} values obtained in acetonitrile. ^{d} Relative ECL efficiencies compared to that of ECL($Ru(bpy)_3{}^{2+}$/TPA) as a reference. ^{e} See ref 3b. ^{f}Relative ECL efficiencies compared to that of ECL($Ru(bpy)_3{}^{2+}$/TPA) as a reference. Anodic peak potential of TPA is between +1.0 and +1.1 V vs SCE.
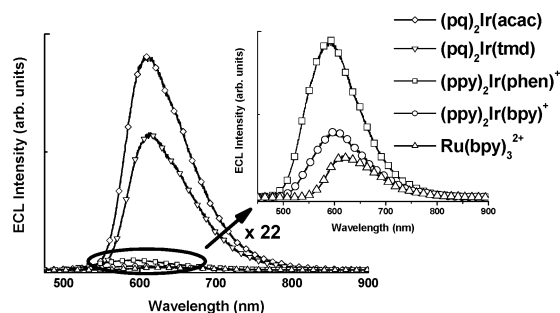
Figure 2. ECL spectra of $Ru(bpy)_3{}^{2+}$, $[(ppy)_2Ir(bpy)]^+$, $[(ppy)_2Ir(phen)]^+$, $(pq)_2Ir(acac)$, and $(pq)_2Ir(tmd)$ in acetonitrile solution (0.1 mM; 10 Hz potential steps from 0 V to $[\epsilon°(ox) + 0.5]$ V vs SCE; 10 s acquisition). Inset: 22 times magnified ECL data for $Ru(bpy)_3{}^{2+}$, $[ppy_2Ir(bpy)]^+$, and $[ppy_2Ir(phen)]^+$.

phosphorescence of complexes is readily visible in the daylight using a hand-held UV light both in the solid state and in solution.

On the basis of the electrochemical properties of the complexes summarized in Table 1, the LUMO level of cationic complexes, $[(ppy)_2Ir(bpy)]^+$ and $[(ppy)_2Ir(phen)]^+$, lower than that of $\epsilon°(TPA^•)$ is expected to accept an electron more efficiently from TPA$^•$ than in the case of fac-$Ir(ppy)_3$, meaning efficient generation of excited states as described in reaction 4. The HOMO level of cationic complexes, $[(ppy)_2Ir(bpy)]^+$ and $[(ppy)_2Ir(phen)]^+$, lower than that of fac-$Ir(ppy)_3$ is expected to accelerate the generation of TPA$^{+•}$ as shown in reaction 2′ by more efficiently removing an electron from a TPA molecule. As expected, $[(ppy)_2Ir(bpy)]^+$ and $[(ppy)_2Ir(phen)]^+$ showed 2 times and 4 times, respectively, higher ECL intensity than the $Ru(bpy)_3{}^{2+}$ system in ECL experiments with TPA as a co-reactant, while the concentrations of the metal complexes remained constant (Figure 2). The $[(ppy)_2Ir(phen)]^+$ complex has oxidation and reduction potentials similar to those of $[(ppy)_2Ir(bpy)]^+$, along with the higher PL quantum efficiency, probably due to the more rigid structure, as proven in $Ru(bpy)_3{}^{2+}$ and $Ru(phen)_3{}^{2+}$ systems. As expected from the similarity of optical and electrochemical properties for the electron transfer and the higher

PL quantum efficiency, $[(ppy)_2Ir(phen)]^+$ gave another 2 times higher ECL intensity than $[(ppy)_2Ir(bpy)]^+$.

Extremely high ECL has been obtained by selecting a neutral 2-phenylquinoline (pqH)-based Ir(III) complex for an emitter, which has a low enough $\epsilon°(ox)$ to effectively generate TPA$^{+•}$ and well-matched $\epsilon°(red)$ to accept electrons more efficiently from TPA$^•$. Under the same concentration of metal complex, $(pq)_2Ir(acac)$ and $(pq)_2Ir(tmd)$ with TPA gave very high ECL compared to a $Ru(bpy)_3{}^{2+}$/TPA system (77 and 49 times for $(pq)_2Ir(acac)$ and $(pq)_2Ir(tmd)$, respectively, as shown in Figure 2). We believe that the efficient electron transfer, controlled by the energetics between the electron donor−acceptor pair, and the relative stability of metal complexes during the ECL measurements could produce these extraordinarily high ECL efficiencies.

In conclusion, we could tune the ECL efficiency of the luminescent metal complex molecules systematically on the basis of the energetic aspect of electron transfer in ECL. By controlling the relative positions of HOMO and LUMO levels (oxidation potential and reduction potential) of Ir(III) complexes, we could obtain high ECL from these complexes in the presence of TPA. To our knowledge, this is the highest ECL intensity ever reported from metal complexes with TPA as a co-reactant. We believe this high ECL efficiency of new Ir(III) complexes can be used in many interesting applications, such as sensors and luminescent devices. It is expected that the sensitivity of ECL sensors can be increased more than 10 times simply by replacing conventional the $Ru(bpy)_3{}^{2+}$ complex with our highly efficient Ir(III) complexes. Details about the application of the Ir(III) complexes in ECL sensors will be reported in a separate paper.

Supporting Information Available: Experimental details for iridium(III) complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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