Electrogenerated Chemiluminescence of a Bis-cyclometalated Alkynylgold(III) Complex with Irreversible Oxidation using Tri-*n*-propylamine as Co-reactant

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Supporting Information

1. Experimental

Chemicals Tri-*n*-propylamine (TPrA, 98%), triisopropanolamine (TPr-OH-A, 98.5%), Zonyl® FSO-100 ($F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_{0-15}H$), and tetra-*n*-butylammonium hexefluorophosphate (^{n}Bu$_4$NPF$_6$, ≥ 99%) were purchased from Sigma-Aldrich. The bis-cyclometalated alkynylgold(III) complex, [Au(C^N^C)(C≡CC$_6$H$_4$NPh$_2$)] (C^N^C = 2,6-diphenylpyridine) **1**, was synthesized and purified according to previously reported procedures.[1-3] Other chemicals were of analytical grade and were used as received. All aprotic solvents were purified and distilled using standard procedures before use. All the aqueous solutions were prepared with deionized water (Milli-Q, Millipore). The pH of the phosphate buffer solution (PBS, 0.15 M) containing TPrA was adjusted with concentrated NaOH or phosphoric acid. The stock solution of **1** (0.2 mM) was prepared with dimethylformamide (DMF) to obtain good solubility, followed by dilution (100-fold) with PBS containing TPrA for the LOP ECL measurements.

Apparatus Cyclic voltammetry (CV) and chronoamperometry (CP) were performed with the model 600A electrochemical workstation (CH Instruments, Austin, TX). The three-electrode system

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consisted of a working electrode, a coiled Pt wire counter electrode, and a saturated calomel electrode (SCE) or Ag/AgCl reference electrode. The ECL signals along with the CV or CP were measured with a photomultiplier tube (PMT, Hamamatsu R928) installed under the electrochemical cell. A voltage of –800 V was supplied to the PMT with the Sciencetech PMH-02 instrument (Sciencetech Inc., Hamilton, Ontario, Canada). UV-Visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. PL spectral measurements were performed on a Spex Fluorolog-2 model F 111 spectrofluorometer. ECL spectral measurements were conducted by using an Oriel InstaSpec V intensified charged-coupled device camera system (model 77195) cooled to –15 °C. Excited-state lifetime of solution sample **1** was measured using a conventional laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence quantum yield of **1** was measured by the optical dilute method reported by Demas and Crosby,[4] using $[Ru(bpy)_3]Cl_2$ as the standard.[5]

Procedures A 3-mm diameter glassy carbon (GC) electrode and a 2-mm diameter gold electrode were polished with 0.05-μm alumina slurry to obtain a mirror surface and then were sonicated and thoroughly rinsed with Milli-Q water. Before measurement in the aprotic solution, the GC electrode was rinsed with CH_2Cl_2 followed by drying in an oven at 50 ºC for 10 min. Before each experiment, the gold electrode was subjected to repeated scanning in a wide potential range in 0.1 M H_2SO_4 solution until reproducible voltammograms were obtained. The modification of the gold electrode with FSO-100 (FSO-Au) was conducted by immersing the electrode in 1 wt % FSO aqueous solution for 5 min, followed by thoroughly rinsing with distilled water to remove any unadsorbed species. Solution pH was adjusted to 7.5 to obtain intense LOP ECL signal.[6] In order to eliminate the influence of oxygen,[7] all solutions were deaerated by bubbling high purity (99.995%) N_2, and a constant flow of N_2 was maintained over the solution during the measurements. All potentials reported were against the SCE reference (The potentials in the aprotic system were calibrated against an aqueous SCE by the addition of ferrocene as an internal standard taking $E°(\text{ferrocene}^{+/0}) = +0.424$ V vs. SCE[8]). All experiments were performed at room temperature.

2. Electronic absorption and photoluminescence spectra

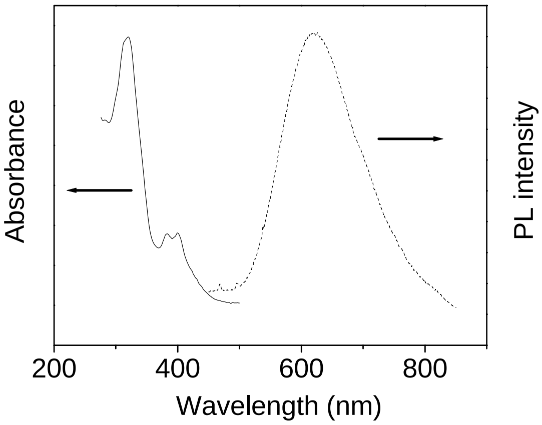

Figure S1. Electronic absorption spectrum (solid line) and photoluminescence (PL) spectrum (dashed line) of **1** in CH_2Cl_2 solution.

3. Annihilation ECL of [Au(C^N^C)(C≡CC$_6$H$_4$NPh$_2$)]

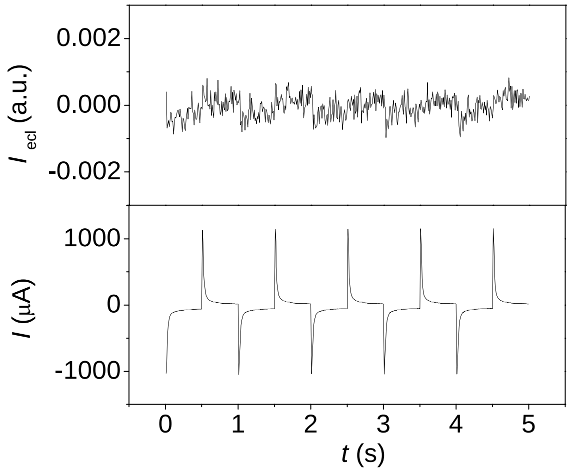

Figure S2. Typical chronoamperometric transient and corresponding ECL curve of **1** (200 µM) in CH_2Cl_2 (0.1 M $^{n}Bu_4NPF_6$). Working electrode, GC. The chronoamperometry settings were high limit of potential pulse, +1.9 V vs. SCE; low limit of potential pulse, –1.7 V vs. SCE; potential pulse width, 0.5 s.

4. Cyclic voltammograms and corresponding ECL curves of [Au(C^N^C)(C≡CC$_6$H$_4$NPh$_2$)] using TPrA as co-reactant in aprotic solution, or using triisopropanolamine (TPr-OH-A) as co-reactant in aqueous solution

The proposed LOP ECL mechanism of **1** could also be further confirmed by the experiment conducted in the aprotic solution. As showed in Figure S3, TPrA started to be oxidized at potentials ~ +0.55 V and showed a maximum oxidation peak at ~ +0.95 V vs. SCE. In contrast to the case in aqueous solution, where a prewave LOP ECL appeared in the potential region of TPrA oxidation due to the formation of excited state on reaction of TPrA$^{\bullet+}$ with the TPrA$^{\bullet}$-reduced [Ru(bpy)$_3$]$^+$ or **1**$^-$, no noticeable corresponding LOP ECL signals were found in the aprotic solution. The abesnce of the LOP ECL signal along with the facile TPrA oxidation has been attributed to the extremely short lifetime of TPrA$^{\bullet+}$ in the aprotic solvent.[6,9] As TPrA$^{\bullet+}$ acts as the crucial intermediate oxidant in the LOP ECL emission, the lifetime of TPrA$^{\bullet+}$ was of great importance.[6] In the potential region (> 1.2 V vs. SCE) where [Ru(bpy)$_3$]$^{2+}$ oxidation occurred, an intense ECL signal was observed, which should be produced by reaction of [Ru(bpy)$_3$]$^{3+}$ with TPrA$^{\bullet}$. However, no noticeable ECL signal was found in the case of **1**, probably because the poor stability of the oxidation product of **1** has significantly hampered such a reaction pathway.

Recent study indicated the usefulness of the tertiary amines with hydroxyl group substituent as [Ru(bpy)$_3$]$^{2+}$ ECL co-reactant.[10] In general, the ECL mechanism developed using TPrA as a co-reactant is probably operative for the hydroxy-substituted tertiary amines. As showed in Figure S4, the oxidation of triisopropanolamine (TPr-OH-A) was similar to that of TPrA, whereas the corresponding ECL profiles revealed remarkable difference. For the [Ru(bpy)$_3$]$^{2+}$/TPr-OH-A system, ECL was produced only when the electrode was scanned to a potential more positive than ~ +1.0 V, where [Ru(bpy)$_3$]$^{2+}$ started to be oxidized. The LOP ECL signal that appeared before [Ru(bpy)$_3$]$^{2+}$ oxidation, however, has not been observed despite the facile oxidation of TPr-OH-A. Similarly, no ECL emission of **1** similar to that found using TPrA as co-reactant was observed in the case of TPr-OH-A. The absence of LOP ECL signal along with the facile oxidation of TPr-OH-A in both cases may be attributed to the fact that TPr-OH-A$^\bullet$ is not energetically powerful enough to reduce $[Ru(bpy)_3]^{2+}$ and **1** due to the strong electron-withdrawing ability of the hydroxy groups.[11,12]

In general, the ECL results of both $[Ru(bpy)_3]^{2+}$ and **1** were consistent with their electrochemical behaviors, indicating the significance of the LOP ECL technique in exploring potential ECL of the luminescent metal complexes with irreversible oxidation but reversible reduction.

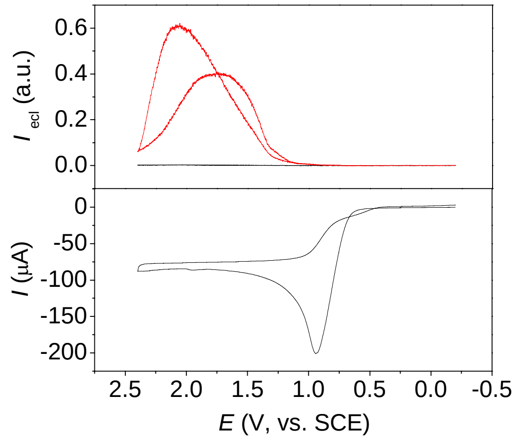

Figure S3. Cyclic voltammogram and corresponding ECL curve obtained at GC electrode. Solution, **1** (2 μM) and TPrA (10 mM) in CH_3CN/CH_2Cl_2 (90:10, v/v) containing 0.1 M $^nBu_4NPF_6$. Scan rate, 100 mVs^{-1}. For comparison, an ECL curve (red line) of $[Ru(bpy)_3]^{2+}$ (2 μM) under the same experimental conditions is also presented. The CV profile (mainly TPrA oxidation) is not included because it is essentially the same as that for the case of **1**.

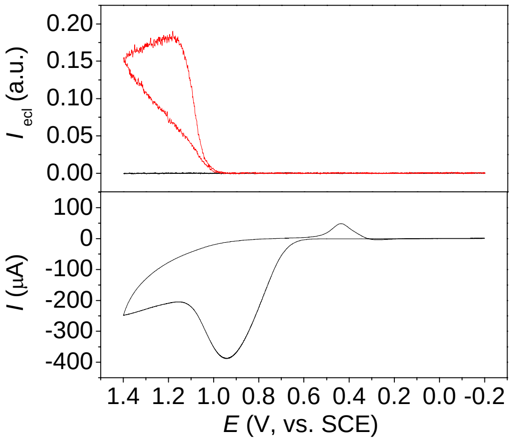

Figure S4. Cyclic voltammogram and corresponding ECL curve obtained at the FSO-Au electrode. Solution, **1** (2 μM) and TPr-OH-A (100 mM) in 0.15 M PBS (pH 7.5, 1 wt % DMF). Scan rate, 100 mVs^{-1}. For comparison, an ECL curve (red line) of $[Ru(bpy)_3]^{2+}$ (2 μM) under the same experimental conditions is also presented. The CV profile (mainly TPr-OH-A oxidation) is not included because it is essentially the same as that for the case of **1**.

Notes and references

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