# **Electronic Supporting Information**

## **Bright electrochemiluminescence of iridium(III) complexes**

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1. Synthesis of  $[(C^N)_2 Ir(N^N)]^+ PF_6^-$  Complexes 1-4



The synthesis and characterization have been published in a previous report.<sup>1</sup>

#### 2. Electrochemical and Photophysical Data Summary

A brief summary of the electrochemical and photophysical data is given below.

| Compound | E <sub>1/2, ox</sub> | $\Delta E_p$ | ΔE     | E <sub>1/2, red</sub> | $\Delta E_p$ |
|----------|----------------------|--------------|--------|-----------------------|--------------|
| 1        | 1.28 V               | 69 mV        | 2.75 V | -1.47 V               | 78 mV        |
| 2        | 1.26 V               | 84 mV        | 2.82 V | -1.56 V               | 84 mV        |
| 3        | 1.61 V               | 105 mV       | 3.01 V | -1.40 V               | 69 mV        |
| 4        | 1.60 V               | 96 mV        | 3.09 V | -1.49 V               | 75 mV        |
| a        |                      |              |        |                       |              |

Table S1. Electrochemical Properties of  $1-4^{a1}$ 

<sup>*a*</sup> Measured in acetonitrile (ca. 1.5 mM) with NBu<sub>4</sub>PF<sub>6</sub> (ca. 0.1 M) as supporting electrolyte. Potentials (V) are reported vs. SCE standard electrode and were calibrated using an internal standard Fc/Fc<sup>+</sup> redox couple (0.40 V in ACN).<sup>2</sup>

| Compound | Photoluminescence (PL, $\lambda_{max}$ ) <sup><i>a</i></sup> | PL Quantum yield $(\phi)^b$ |
|----------|--|-----------------------------|
| 1        | 580 nm   | 25.1                        |
| 2        | 575 nm   | 34.6                        |
| 3        | 514 nm   | 73.1                        |
| 4        | 498 nm   | 79.7                        |

Table S2. Photophysical Properties of  $1-4^{1}$ 

<sup>*a*</sup> Measured in acetonitrile at 298 K. <sup>*b*</sup> Measured at 298 K using Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>  $\phi = 9.5 \%^3$  in acetonitrile.

#### 3. General Procedures for ECL Studies of Compounds 1-4

For annihilation ECL studies, approximately 2 mg of compound (1-4) was added to a pyrex electrochemical cell with a flat Pyrex window at the bottom for detection of generated ECL, containing 0.1 M TBAPF<sub>6</sub> (tetrabutylammonium hexafluorophosphate) supporting electrolyte in anhydrous acetonitrile (3 mL) that was assembled in a dry box. For coreactant studies,  $5.0 \times 10^{-3}$  M BPO was added to the annihilation solution and assembled in a dry box. A 2 mm diameter Pt disc inlaid in a glass sheath were used as the working electrode (WE), a coiled Pt wire as the counter electrode (CE), and a coiled Ag wire as the quasi reference electrode (RE), respectively. Routine cleaning procedures for the electrodes and cell were reported elsewhere. <sup>4, 5</sup>

For detailed electrochemical workstation and ECL setup information, please refer to our previous publications.<sup>4, 5</sup>

In brief, the cyclic voltammetry was conducted on a CHI 610A electrochemical analyzer (CH Instruments, Austin, TX). The experimental parameters for cyclic voltammograms (CVs) are listed here: 0.000 V initial potential in experimental scale, positive or negative initial scan polarity,  $0.1 \text{ Vs}^{-1}$  scan rate, 4 sweep segments, 0.001 V sample interval, 2 s quiet time,  $1-5 \times 10^{-5} \text{ AV}^{-1}$  sensitivity. Potentials (V) were calibrated using an internal standard Fc/Fc<sup>+</sup> redox couple (0.40 V in ACN)<sup>2</sup> after each experiment, and are reported vs. SCE standard electrode.

The ECL data along with CV data were obtained using the CHI 610A coupled with a photomultiplier tube (PMT, R928, Hamamatsu, Japan) held at -750 V with a high voltage power supply. The ECL collected by the PMT under the flat Pyrex window at the bottom of the cell was measured as a photocurrent, and transformed to a voltage signal, using a picoammeter/voltage source (Keithley 6487, Cleveland, OH). The potential, current signals from the electrochemical workstation, and the photocurrent signal from the picoammeter were sent simultaneously through a DAQ board (DAQ 6052E, National Instruments, Austin, TX) in a computer. The data acquisition system was controlled from a custom-made LabVIEW program (ECL\_PMT610a.vi, National Instruments, Austin, TX). The photosensitivity on the picoammeter was set manually in order to avoid the saturation.

ECL pulsing experiments were conducted by using a potentiostat (Model AFCBPI, Pine Instrument Co., Grove City, PA), an EG&G PAR 175 Universal Programmer (Princeton Applied Research, Trenton, NJ), and the PMT with the picoammeter in the similar manner. The assembly was able to perform the pulsing experiments without a delay in a relative fast time pace. The data acquisition for the current, potential and ECL signals was carried out using another homemade LabVIEW program (ECL\_PAR610a.vi). For coreactant systems, the applied potential was pulsed at the WE in the cathodic region (in the experimental potential scale between 0 and low

limit potential value for the compound reduction as obtained from CV experiments) with a pulse width of 0.1 s or 10 Hz.

The ECL spectra were obtained by replacing the PMT with a spectrometer (Cornerstone 260, Newport, Canada) attached to a CCD camera (Model DV420-BV, Andor Technology, Belfast, UK). The camera was cooled to -55 °C prior to use, and controlled by a computer for operation and data acquisition. The intensities versus wavelengths (spectra) were recorded by Andor Technology program. Similar to the pulsing experiments, the samples were pulsed at 10 Hz within each compound's potential window.

ECL quantum efficiencies (QE) were calculated relative to  $[Ru(bpy)_3](PF_6)_2$  taken as 100% in acetonitrile solution (absolute quantum ECL efficiency of  $[Ru(bpy)_3]^{2+}$  is  $0.05^{6, 7}$ ) by integrating both the ECL intensity and current value versus time for each compound, as described in Equation (S1),

$$\Phi_{x} = 100 \times \left(\frac{\int_{a}^{b} ECLdt}{\int_{a}^{b} Currentdt}\right)_{x} / \left(\frac{\int_{a}^{b} ECLdt}{\int_{a}^{b} Currentdt}\right)_{st}$$
(S1)

where x stands for the compound (1-4) and st represents  $[Ru(bpy)_3](PF_6)_2$ .





Fig. S1 CV of **4** with varying scan rate from 0.06 V/s to 0.18 V/s.



Fig. S2 CV of  $[Ru(bpy)_3](PF_6)_2$  with varying scan rate from 0.04 V/s to 0.20 V/s.



Fig. S3 Plot of anodic peak current,  $i_{pa}$ , of **4** against  $v^{1/2}$  (v = scan rate).



Fig. S4 Plot of cathodic peak current,  $i_{pc}$ , of **4** against  $v^{1/2}$  (v = scan rate).



Fig. S5 Plot of anodic peak current,  $i_{pa}$ , of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> against  $v^{1/2}$  (v = scan rate).



Fig. S6 Plot of cathodic peak current,  $i_{pc}$ , of  $[Ru(bpy)_3](PF_6)_2$  against  $v^{1/2}$  (v = scan rate).



5. Cyclic Voltammograms and ECL-Voltage Curves in the Coreactant Path

Fig. S7 Cyclic voltammograms (dotted lines) overlaid with the ECL-voltage curves (solid lines) of compounds **1-4** in the coreactant path.

#### 6. Supplementary Video and Photograph

Please see the attached video in the ESI of complex **3** emitting green electrochemiluminescence when pulsing between its oxidation and reduction potentials at the working electrode.

In addition, please refer to the photograph of the ECL cell with complex **3** in solution under UV illumination.

### References

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