Electronic Supplementary Information for

Correlating electronic structures to electrochemiluminescence of cationic Ir complexes

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Experimental Procedures

Electrochemical preparation. CV, DPV, and ECL experiments were conducted using a 2 mm diameter Pt disc inlaid in a glass sheath as the working electrode (WE), a coiled Pt wire as the counter electrode (CE), and a coiled Pt wire as the quasi reference electrode (RE). Cleaning procedures have been previously reported.[1] All solutions for electrochemical and ECL experiments were prepared in the electrochemical cell, placed inside an N_2-filled drybox that possessed little oxygen and moisture. The solutions of complexes **1-4** studied had concentrations of approximately $1.2 \times 10^{-\square}$ M for **1**, $6.6 \times 10^{-\square}$ M for **2**, $9.2 \times 10^{-\square}$ M for **3**, and $6.3 \times 10^{-\square}$ M for **4**, in anhydrous acetonitrile (Sure/Seal^{TM} bottle from Aldrich) containing 0.1 M $TBAPF_6$ as supporting electrolyte. The electrodes were immersed in the solution and connected by copper wire inserted through the air-tight Teflon cap. The assembly was moved out of the drybox to perform electrochemistry and ECL experiments. After completion of each experiment, the electrochemical potential window was calibrated using Fc as the internal standard. The redox potential of Fc/Fc^+ was taken as 0.40 V *vs*. SCE.[2]

Electrochemical instrumentation. The CVs were conducted on a CHI 610A electrochemical analyzer (CH Instruments, Austin, TX). The experimental parameters for CVs are listed here: 0.000 V initial potential in experimental scale, negative initial scan polarity, 0.1 V/s scan rate, 4 sweep segments, 0.001 V sample interval, 2 s quiet time, 1×10^{-5} AV^{-1} sensitivity. The potential range depended on the particular complex.

ECL instrumentation. The ECL cell was specifically designed to have a flat Pyrex window at the bottom for detection generated light from the WE and was sealed with a Teflon cap with a rubber O-ring for CV and ECL measurements. 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 for complex **1** 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 a 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). The applied potential was pulsed at the WE between 1.52 V and -1.92 V with a pulse width of 0.1 s or 10 Hz for 30 s.

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 CV experiments, the samples were scanned at 0.1 V/s, within each complex's potential window. The exposure time of the spectra was set to the amount of time for two complete scans. Vertical lines/spikes observed in the spectra were from cosmic rays from the CCD camera.

For the spooling experiments, the same spectrometer and CCD camera were used and the following parameters were employed in the Andor Technology program under the kinetic parameters option tab: for complex **4**: exposure time = 1 s, number of accumulations = 1, kinetic series length = 130 s (matching with the potential scan time for two complete cycles), kinetic cycle time = 1, and the spectrometer was centered at 600 nm using the 121.6 l/mm grating, with the camera cooled to -55 °C. On the CHI 610A electrochemical analyzer, the initial potential was set to 0.00 V, high potential = 1.84 V, low potential = -1.73 V, sensitivity = 1×10^{-5} AV^{-1}, initial scan polarity = negative, scan rate = 0.1 V/s sweep segments = 4, sample interval = 0.001 V, quiet time 2 s. Simultaneously, the CHI 610A electrochemical analyzer and the Andor Technology program were run and the CV and spooling spectra were collected.

ECL efficiency calculations. ECL quantum efficiencies (QE) were calculated relative to $[Ru(bpy)_3](PF_6)_2$ (the reported absolute ECL efficiency, Φ_{ECL}, of $Ru(bpy)_3^{2+}$ is 0.05)[3, 4] by integrating both the ECL intensity and current value versus time for each compound, as described in Equation (S1)[1, 5, 6],

$$\Phi_x = 100 \times \left(\frac{\int_a^b ECLdt}{\int_a^b Currentdt} \right)_x \Bigg/ \left(\frac{\int_a^b ECLdt}{\int_a^b Currentdt} \right)_{st} \qquad \text{(S1)}$$

where x stands for the complex (**1-4**) studied, a and b represents the integral time range, and st represents $[Ru(bpy)_3](PF_6)_2$.

References

1. K. N. Swanick, D. W. Dodd, J. T. Price, A. L. Brazeau, N. D. Jones, R. H. E. Hudson and Z. Ding, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17405-17412.
2. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.
3. P. McCord and A. J. Bard, *J. Electroanal. Chem.*, 1991, **318**, 91-99.
4. J. E. Bartelt, S. M. Drew and R. M. Wightman, *J. Electrochem. Soc.*, 1992, **139**, 70-74.
5. D. Laser and A. J. Bard, *J. Electrochem. Soc.*, 1975, **122**, 632-640.
6. W. L. Wallace and A. J. Bard, *J. Phys. Chem.*, 1979, **83**, 1350-1357.