Electronic Supplementary Information For:

Confirmation of the Classic Tris(2,2′-bipyridyl)ruthenium(II) and Oxalate Electrochemiluminescence Mechanism using EPR Spectroscopy

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Experimental Details

EPR Spectroscopy

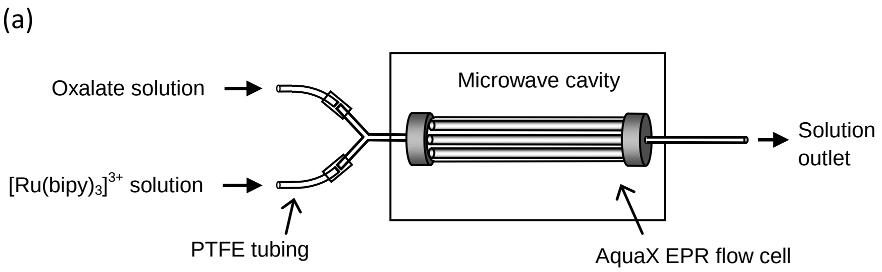
‡ X-Band EPR spectra (Figs. 1, S1 and S3) were recorded on a Bruker Elexsys E580 X-band EPR spectrometer fitted with a Super High Q cavity and an AquaX flow through cell. Calibration of the magnetic field and microwave frequency were achieved with a Bruker ER 036M Teslameter and a Bruker microwave frequency counter, respectively. Continuous flow EPR experiments (ESI schematic a) were performed at the flow rates reported in the text using a Gilson Minipuls 3 peristaltic pump with PVC pump tubing (DKSH, Caboolture, Qld, Australia) connected to PTFE tubing before merging and entering an AquaX cell placed in the microwave cavity. Low temperature (150K) experiments (Fig S1) were performed using the spectrometer described above in conjunction with a nitrogen flow through system controlled by a VT4131 Eurotherm temperature controller.

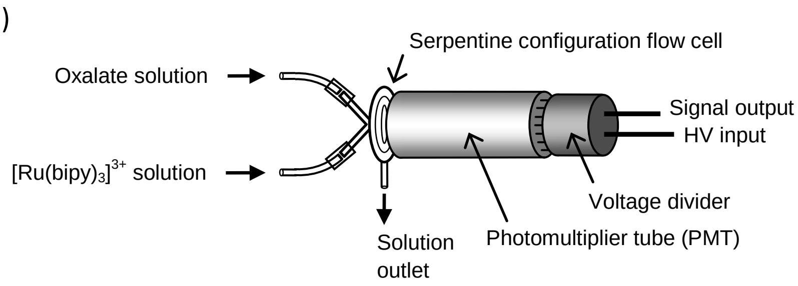
¶ The EPR spectrum (Fig. 1b) of the "120 G" radical was digitised from reference 14a and in the absence of any information concerning the microwave frequency (on a Varian E109 EPR spectrometer the microwave frequency, if accurate, can only be measured to three significant figures) and magnetic field calibration, the magnetic field axis was aligned with our experimental spectrum. The authors thank Dr C.J. Noble (Universtiy of Queensland) for his assistance in formatting the digitised data for computer simulation studies.

Chemiluminescence Spectroscopy

Chemiluminescence measurements were made using the same flow apparatus except reagents were merged in a GloCel detector with a dual-inlet serpentine-channel reaction zone (Global FIA, Fox Island, WA, USA) housed in a light-tight box where emission was recorded using a photomultiplier module (Electron Tubes model P30A 05; ETP) such that the chemiluminescence intensity was continuously monitored over time (ESI: Schematic b).

Experimental Schematic for (a) EPR (Figs. 1, 2) and (b) Chemiluminescence (Fig. S2) spectroscopy.





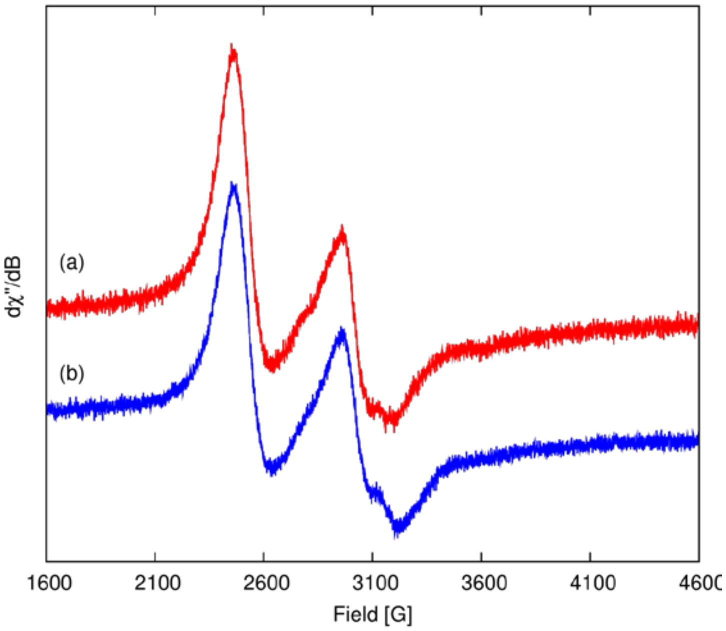


Figure S1. EPR spectra of (a) $[Ru(bipy)_3]^{3+}$ (1 mM, 0.02 M H_2SO_4), ν = 9.428761 GHz, T = 150 K; (b) a solution containing $[Ru(bipy)_3]^{3+}$ (1 mM, 0.02 M H_2SO_4) and oxalate (5 μM), rapidly frozen. ν = 9.429229 GHz, T= 150K.

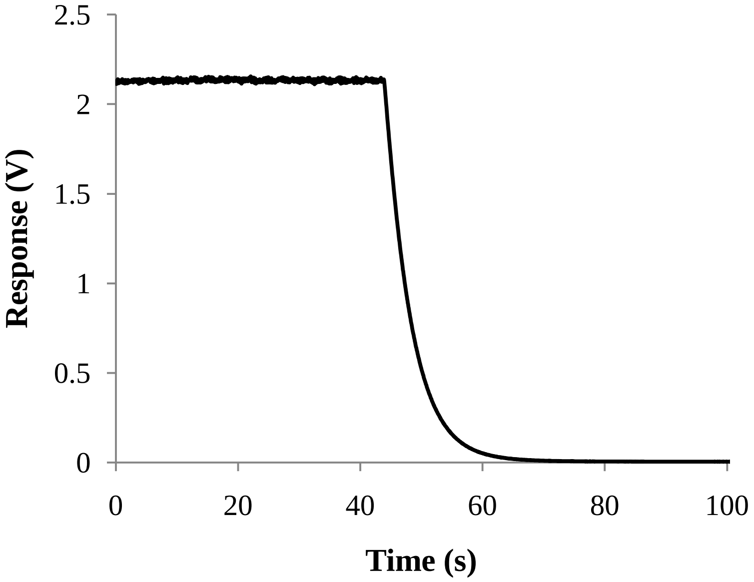


Figure S2. Chemiluminescence emission from the reaction between Ru(bipy)$_3^{3+}$ (1 mM, 0.02 M H_2SO_4) and oxalate (5 µM). The reagents were continuously merged in a dual inlet serpentine flow-cell between t = 0 s and t = 42 s (combined flow rate 6 mL min^{-1}). The continuous flow assembly was stopped at t = 42 s, at which time an almost immediate and rapid decay in emission was observed. **NB.** The oxalate solution was diluted 200-fold compared to EPR experiments (oxalate = 1 mM) to prevent overloading of the photomultiplier tube.

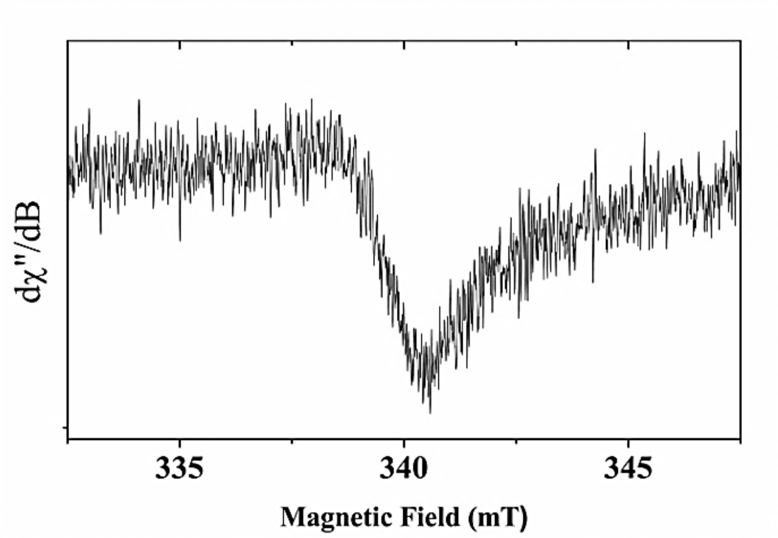


Figure S3. X-band EPR spectrum (mod. amp. = 2G, microwave power = 20 mW, 32 scans) of the reaction between [Ru(bipy)$_3$]$^{3+}$ (1 mM, 0.02 M H_2SO_4) and oxalate (1 mM) at a combined flow rate of 8 mL min^{-1}.