Supporting Information for

A potential-controlled switch on/off mechanism for selective excitation in mixed electrochemiluminescent systems

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Experimental details

Tris[2-phenylpyridinato-C^2,N]iridium(III) (Ir(ppy)$_3$, 99%), tris[2-(4,6-difluorophenyl)pyridinato-C^2,N]iridium(III) (Ir(df-ppy)$_3$, 96%), TPA (98%), TBAPF$_6$ (99.5%, electrochemical grade) were purchased from Sigma-Aldrich (Australia). The synthesis and characterization of bis(2,2′-bipyridine-κN1, κN1′)[1,1′-dimethyl-N,N′-[([2,2'-bipyridine]-4,4′-diyl-κN1, κN1′)dicarbonyl]bis[L-alaninate]]ruthenium(II) hexafluorophosphate ([Ru(bpy)$_2$(L)](PF$_6$)$_2$) has been previously described.[1] Acetonitrile was distilled over calcium hydride drying reagent under grade 5 argon, and solutions were degassed with argon. Tripropylamine (TPA) was distilled under vacuum over NaOH.

Electrochemical experiments were performed with either a CH Instruments (Texas, USA) CH660B (Cyclic voltammograms), Autolab (Metrohm Autolab B.V., Netherlands) PGSTAT12 (Chronoamperometrey & CV with CCD ECL detection), or μAutolab (Chronoamperometry with PMT ECL detection) potentiostat. For all ECL experiments, a 3-electrode electrochemical cell was used, comprising a 3 mm glassy carbon working electrode, Ag/AgNO$_3$ (20 mM) (CH Instruments), non-aqueous reference electrode and gold wire counter electrode. The electrodes were positioned within the quartz cell so as to maximize collection of light through the base. ECL detection: Emission spectra were captured using an Ocean Optics QE65000 spectrometer, interfaced with our electrochemical cell using an optical fiber (1.0 m, 1.5 mm core diameter), with a collimating lens, via a custom cell holder. For some experiments, ECL was detected using an Electron Tubes model 9828B PMT (ET enterprises, UK) biased at 500 V. The electrochemical cell was located within a custom light-tight faraday cage for all ECL experiments. Photoluminescence: Emission spectra were collected using a Varian (Varian, Australia) Eclipse spectrofluorimeter using quartz cells with a 1 cm path length. 3D ECL emission matrix experiments were conducted under argon bubbling using the PGSTA12 potentiostat and QE65000 CCD spectrometer as described previously.[2] The integration time per spectrum was 2 s (resolution = 50 mV per spectrum), facilitated by a relatively slow scan rate of 25 mV/s. The data for each graph was the sum of four or five CV sets and 3D data were smoothed using a Fourier transform algorithm. The lower co-reactant ECL efficiency of Ir(ppy)$_3$ was compensated for by using a larger concentration of this complex in the binary mixtures.

Table S1 Electrochemical and photoluminescence data.

	Potentials vs. Fc[a]				**Photoluminescence**
	$\mathbf{E_{ox}}$	$\mathbf{E_{red}}$	$\mathbf{E^*_{ox}}$[c]	$\mathbf{E^*_{red}}$[c]	$\boldsymbol{\lambda_{max}}$[d]
$Ir(ppy)_3$	0.33	-2.70	-2.1	-0.30	520
$[Ru(bpy)_2(L)]^{2+}$	0.96	-1.47	-0.90	0.39	666
$Ir(df\text{-}ppy)_3$	0.69	-2.51	-1.82	0.00	495
$TPA/TPA^{\bullet+}$	(0.43)[b]	-	-	-	-
$TPA^{\bullet}$	-	-2.09	-	-	-

[a] Fc = 0.39 vs SCE; [b] peak potential from SWV, (see Fig S9); [c] Estimated from ground state redox potentials and RT emission maxima. [d] Corrected for wavelength dependence of detector response.

Abbreviations: ppy = 2-phenylpyridinato; bpy = 2,2′-bipyridine; L = N^4,$N^{4'}$-bis((2S)-1-methoxy-1-oxopropan-2-yl)-2,2′-bipyridyl-4,4′-dicaboxamide); df-ppy = 2-(2,4-difluorophenyl)pyridine); Fc = ferrocene; TPA = tripropylamine.

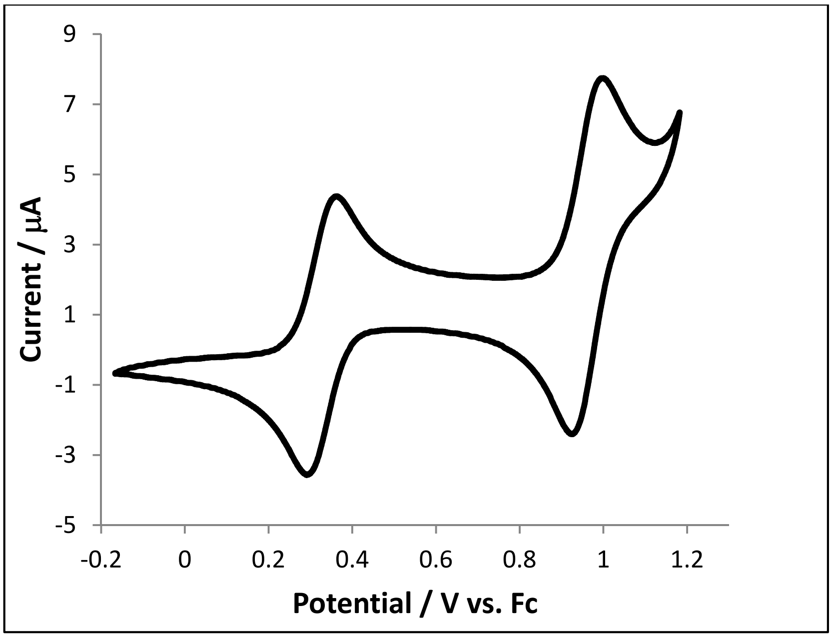

Figure S1 Cyclic voltammetric response for mixture of 0.25 mM Ir(ppy)$_3$ and 0.25 mM [Ru(bpy)$_2$(L)]$^{2+}$ dissolved in acetonitrile containing 0.1 M TBAPF$_6$ as supporting electrolyte (system A). The scan rate was 0.1 V s^{-1} and the working electrode was a 3 mm diameter boron doped diamond disc electrode.

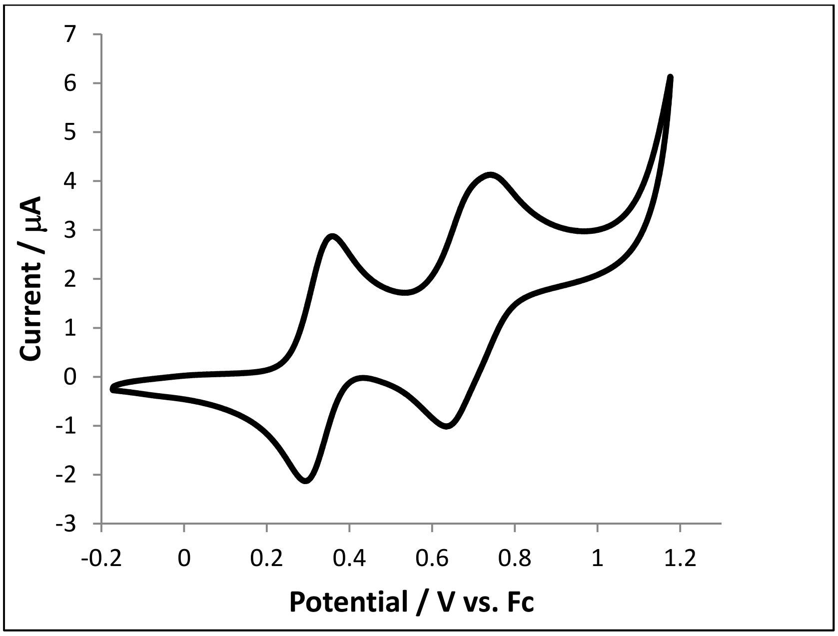

Figure S2 Cyclic voltammetric response for mixture of 0.25 mM Ir(ppy)$_3$ and 0.25 mM Ir(df-ppy)$_3$ dissolved in acetonitrile containing 0.1 M TBAPF$_6$ as supporting electrolyte (system B). The scan rate was 0.1 Vs^{-1} and the working electrode was a 3 mm diameter boron doped diamond electrode.

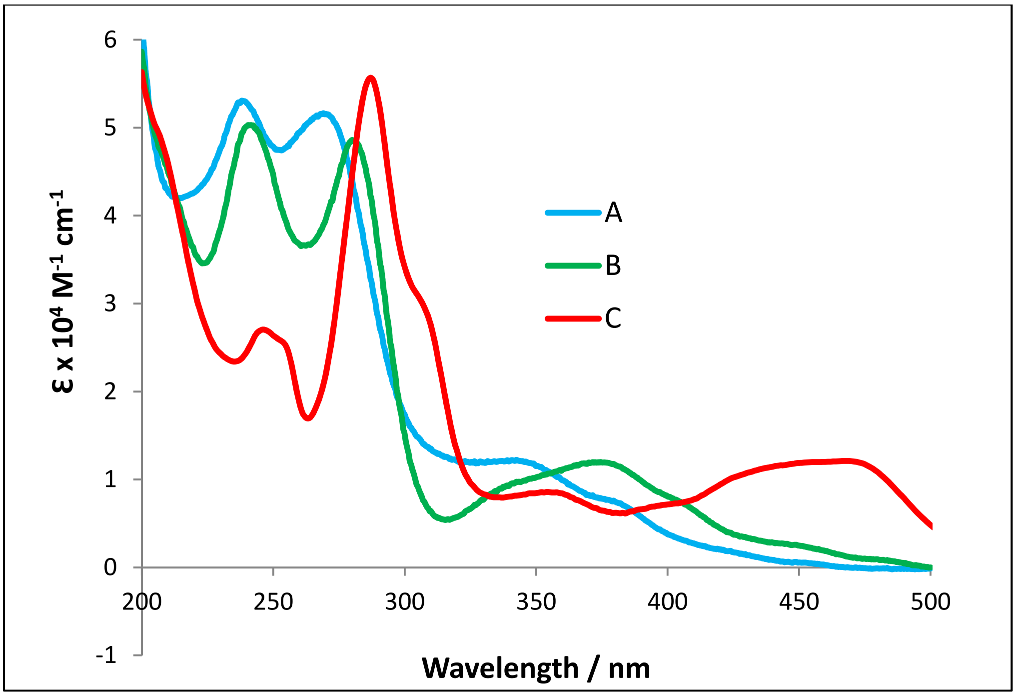

Figure S3 UV-Visible absorption spectra of (A) Ir(df-ppy)$_3$, (B) Ir(ppy)$_3$ and (C) [Ru(bpy)$_2$(L)]$^{2+}$, concentration 10 µM in acetonitrile.

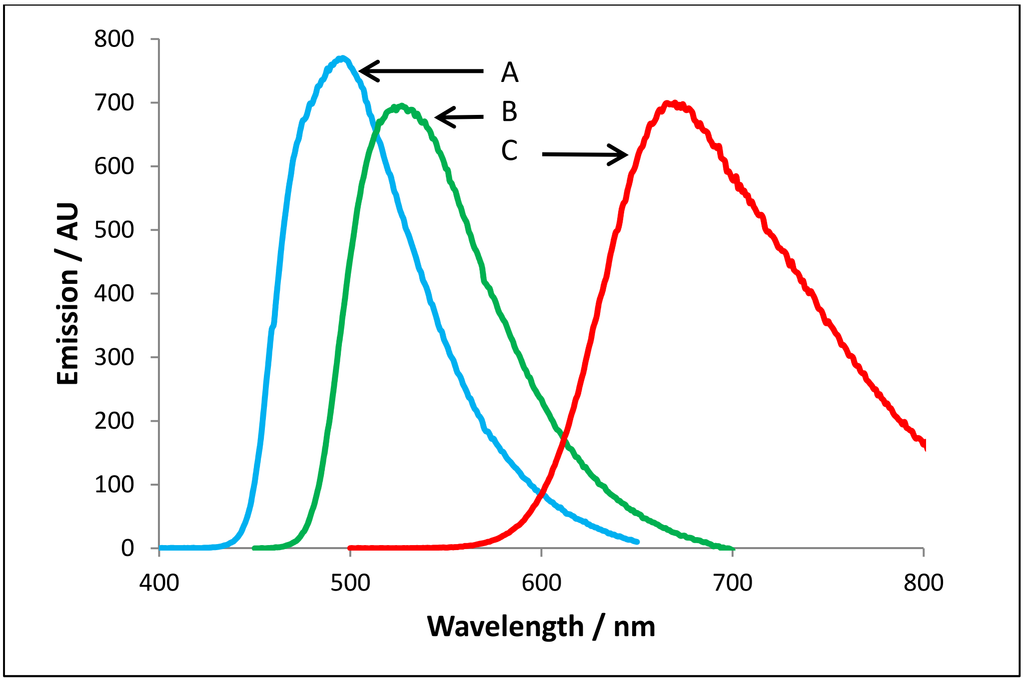

Figure S4 Corrected photoluminescence spectra of (A) Ir(df-ppy)$_3$, (B) Ir(ppy)$_3$, and (C) [Ru(bpy)$_2$(L)]$^{2+}$ in acetonitrile. Excitation wavelength 280 nm, concentration 10 µM. [Ru(bpy)$_2$(L)]$^{2+}$ intensity normalized to Ir(ppy)$_3$.

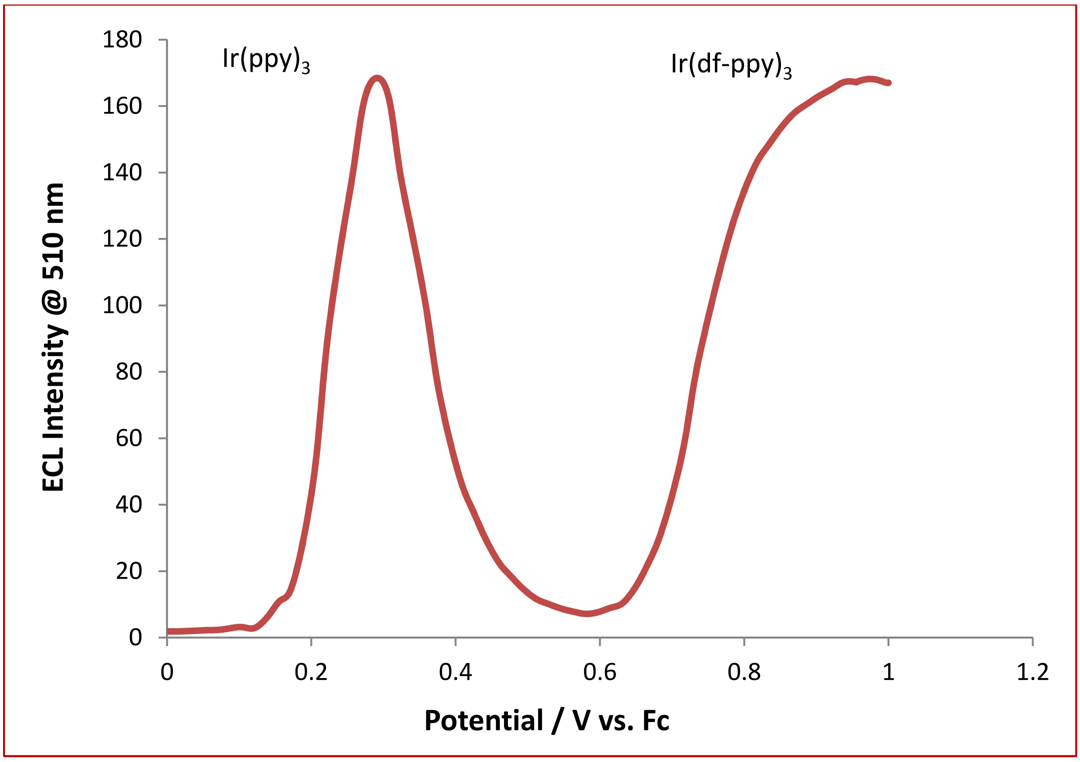

Figure S5 An ECL - potential profile for system B (mixture of Ir(ppy)$_3$ and Ir(df-ppy)$_3$). This is a cross section of Figure 3 at wavelength mid-way between the two emission maxima.

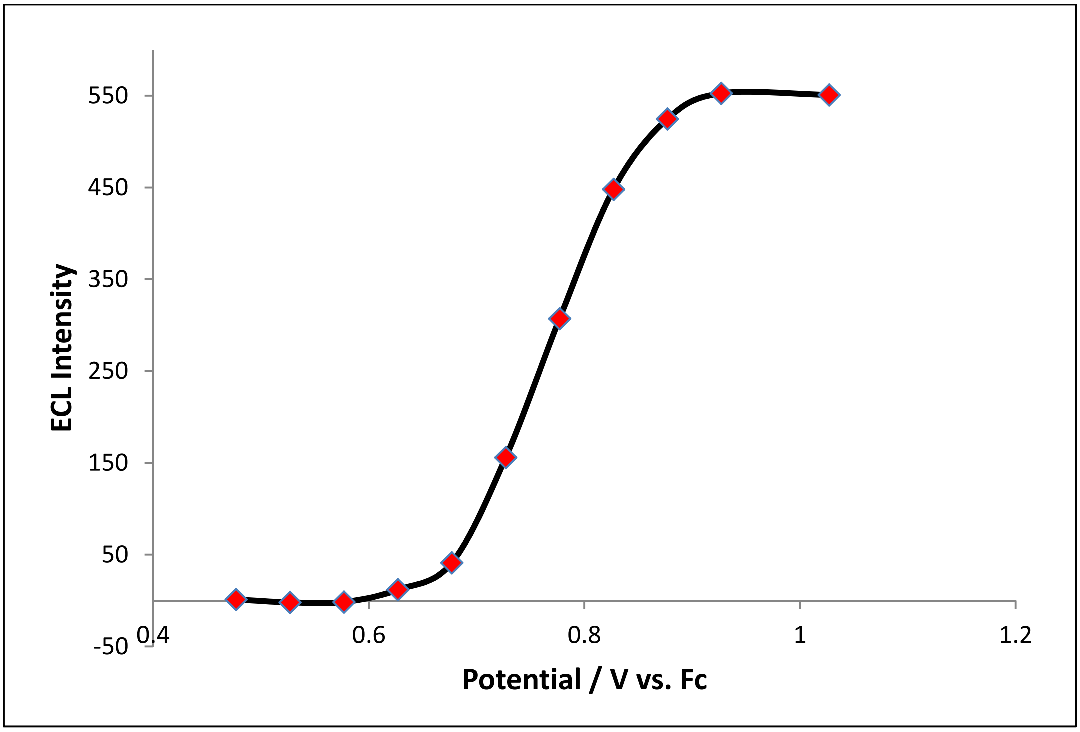

Figure S6 Integrated ECL intensity as a function of applied potential from solution containing 0.1 mM Ir(df-ppy)$_3$ and 10 mM TPA only. Chronoamperometry was used to elicit the ECL emission.

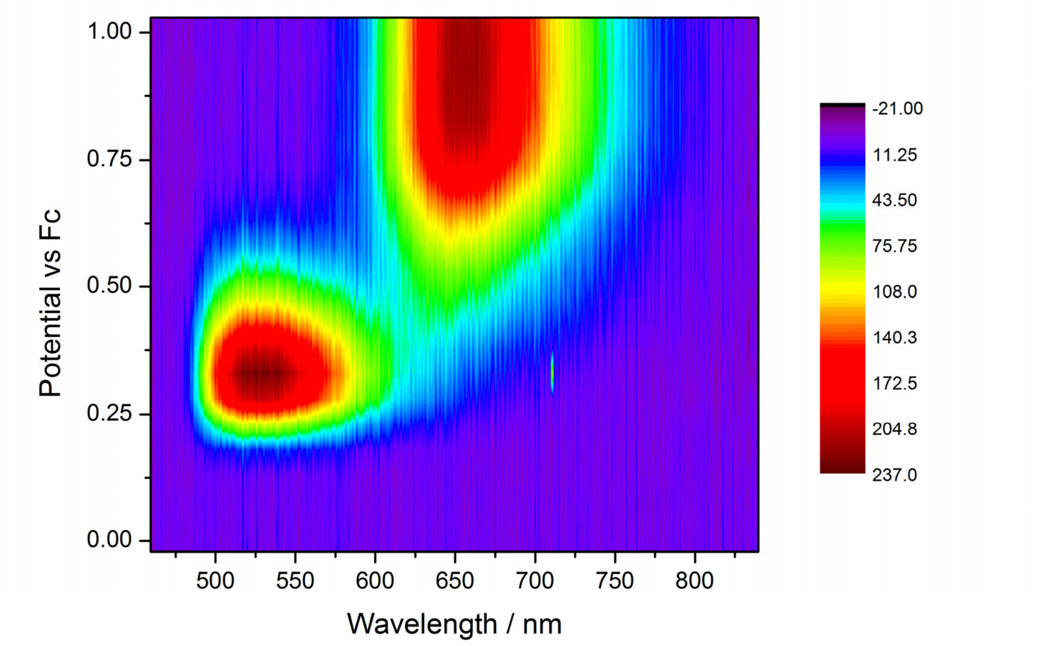

Figure S7 Raw data corresponding to Figure 2 in the main text. 3D-ECL emission matrix for system A (mixture of 0.34 mM Ir(ppy)$_3$ and 0.016 mM [Ru(bpy)$_2$(L)]$^{2+}$, in the presence of 20 mM TPA), during a CV potential sweep from 0 to 1.03 V vs. ferrocene. Scan-rate = 0.025 V/s, spectral integration time = 2 s (resolution = 50 mV per spectrum), data is the sum of 5 CV sets.

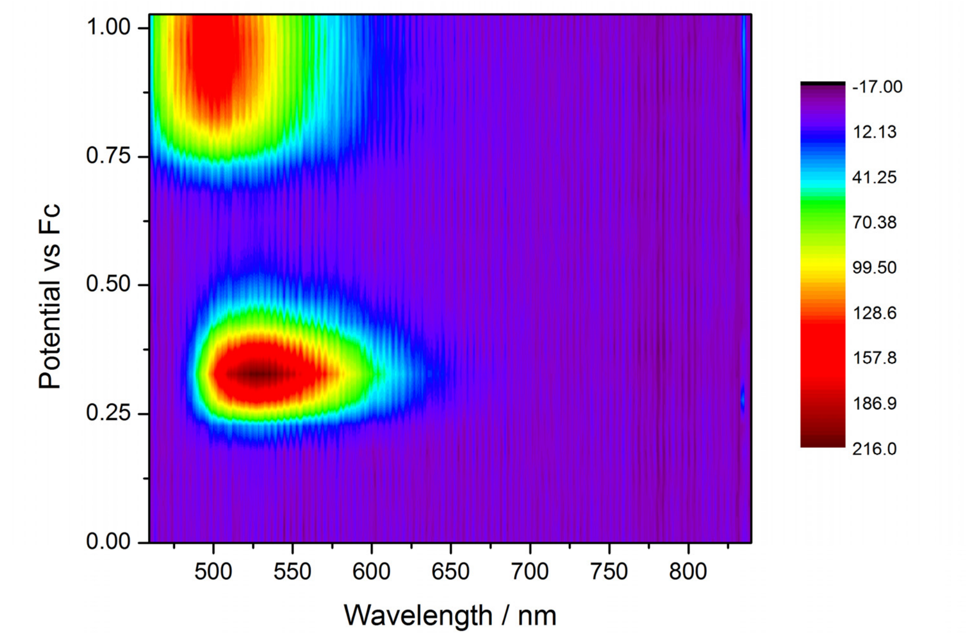

Figure S8 Raw data corresponding to Figure 3 in the main text. 3D-ECL emission matrix for system B (mixture of 0.11 mM Ir(ppy)$_3$ and 0.14 mM Ir(df-ppy)$_3$, in the presence of 20 mM TPA), during a CV potential sweep from 0 to 1.03 V vs. ferrocene. Scan-rate = 0.025 V/s, spectral integration time = 2 s (resolution = 50 mV per spectrum), data is the sum of 4 CV sets.

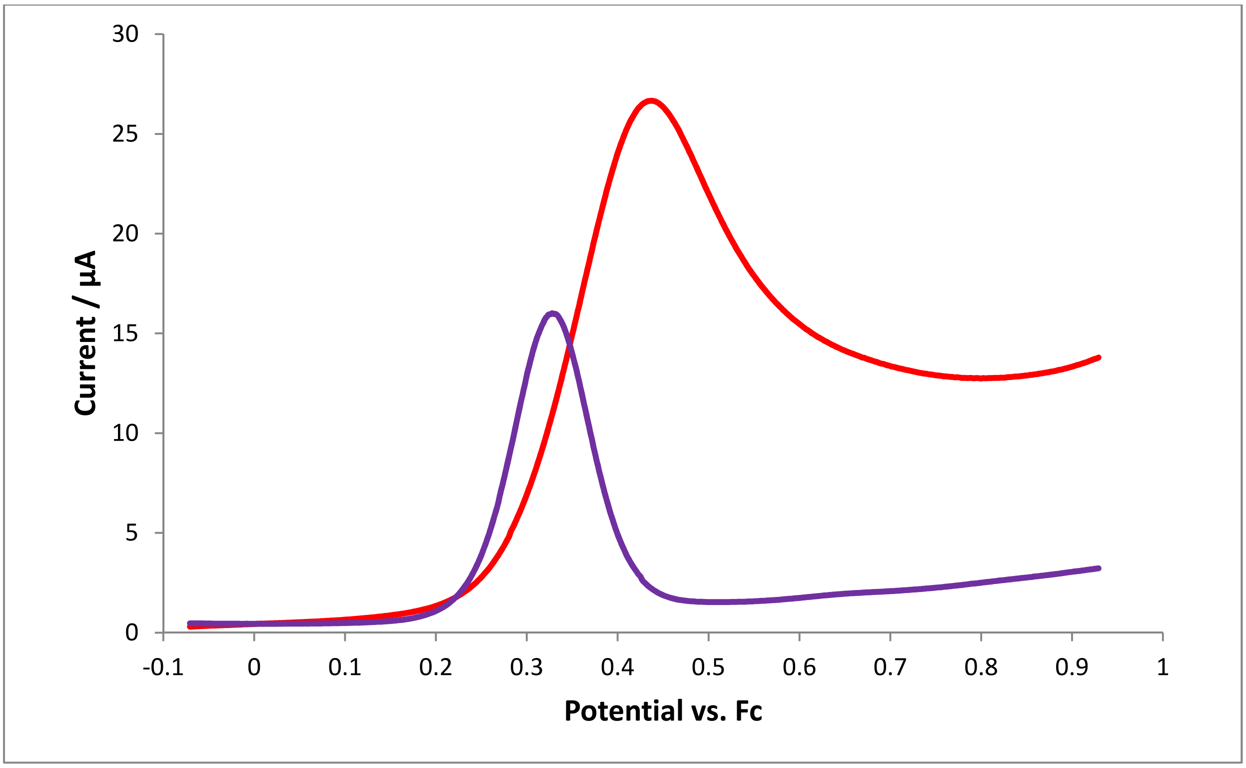

Figure S9: Square wave voltammograms of solutions of 0.25 mM Ir(ppy)$_3$ (purple line) and 1 mM TPA (red line, separate solution) in CH_3CN, the supporting electrolyte was 0.1 M $TBAPF_6$. Amplitude: 0.025V, Frequency: 15Hz.

References

1. G. J. Barbante, C. F. Hogan, D. J. D. Wilson, N. A. Lewcenko, F. M. Pfeffer, N. W. Barnett and P. S. Francis, *Analyst*, 2011, **136**, 1329.
2. E. H. Doeven, E. M. Zammit, G. J. Barbante, C. F. Hogan, N. W. Barnett and P. S. Francis, *Angew. Chem. Int. Ed.*, 2012, **124**, 4430.