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Colour tuning and enhancement of gel-based electrochemiluminescence devices utilising Ru(II) and Ir(III) complexes

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Lachlan C. Soulsby,^a Egan H. Doeven,^b Tien T. Pham,^a Daniel J. Eyckens,^c Luke C. Henderson,^c Benjamin M. Long,^{a,d} Rosanne M. Guijt,^b Paul S. Francis^{*a}

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Combining luminophores in ratios that compensate for energy transfer provides a readily selectable range of new emission colours for gel-based electrochemiluminescence devices (ECLDs). A novel blue ECLD luminophore is also introduced and shown to enhance the intensity of the conventional green emitter through a mixed annihilation ECL mechanism. Peak-to-peak voltages were minimised using asymmetric potential pulse sequences, which increased the longevity of the ECLD emission.

Polymer/ionic-liquid gel-based electrochemiluminescence devices (ECLDs) have emerged as a promising alternative to traditional light-emitting electrochemical cells (LECs) and other electroluminescent systems.¹ Unlike the sequential ‘hopping’ of electrons between the essentially immobile luminophores of LECs, the light producing electron-transport processes in ECLDs involve movement of electrochemically oxidised and reduced luminophores generated by an AC waveform.² This annihilation ECL process³ provides much faster emission turn-on times (0.2–0.3 ms vs 1 min) but lower emission intensities than LECs. Consequently, considerable effort has been invested into enhancing the efficiency of ECLDs. For example, Moon *et al.*⁴ varied the physical properties of the gel by altering the alkyl chain length on the imidazolium ion of the ionic liquid. Shorter chain lengths provided faster turn-on times and greater luminance, due to the lower viscosity and higher conductivity of the gels. The influence of the applied potentials has been examined, including their magnitude and frequency,^{1a,5} and the relative length of the oxidative and reductive pulse.^{5c}

Various luminophores have been explored for ECLDs, including red ([Ru(bpy)₃]Cl₂/[Ru(bpy)₃](PF₆)₂),^{1a,4,5a,5d,6} yellow ([Ir(ppy)₂(bpy)](PF₆)),⁷ green ([Ir(df-ppy)₂(bpy)](PF₆))^{1a,4,5d} and blue (9,10-diphenylanthracene (DPA))^{5d} emitters. However, with a diverse range of charge and structure, the nature and performance of these electrochemiluminophores within gel matrices under applied potentials vary widely.^{5d}

Noting the multi-coloured co-reactant ECL of mixtures of metal complexes in solution,⁸ Moon *et al.* combined red ([Ru(bpy)₃]Cl₂) and green ([Ir(df-ppy)₂(bpy)](PF₆)) luminophores at mole ratios from 20:80 to 80:20 in ECLDs.^{1a} Unlike the previous studies, only the characteristic red emission from the Ru(II) complex was observed, with up to a two-fold enhancement in intensity, due to efficient electron transfer between ECL systems. Subsequent investigations⁹ of annihilation ECL from mixtures of metal complexes in acetonitrile, however, showed simultaneous emission from both luminophores when the red emitter was included in much lower proportions.

Herein, we show that the colour of ECLD emission can be finely tuned through the ratio of emissions from two luminophores. We also implement an asymmetric AC waveform with oxidative and reductive pulses of different magnitude as a new approach to increase ECLD emission lifetimes, and we enhance the green emission of [Ir(df-ppy)₂(bpy)](PF₆) by introducing a novel blue luminophore for ECLD.

The devices were fabricated in a similar manner to those previously described.^{1a,4,5a} The luminophore ([Ru(bpy)₃](PF₆)₂, [Ir(df-ppy)₂(bpy)](PF₆) or [Ir(df-ppy-CF₃)₂(ptb)](PF₆); Fig. S1), polymer (P(VDF CO HFP) dissolved in acetone) and ionic liquid ([BMIM][TFSI]) were combined in a 1:4:16 mass ratio and set on ITO glass. Insulation tape was then placed over a portion of the gel and ITO, and silver conductive paint was applied to form an upper electrode (Fig. 1). A potentiostat was used to apply the potentials. As a simple approach to measure emission intensity and colour, the ECLD emission was recorded using a digital camera (controlled by the potentiostat),¹⁰ positioned 15 cm

^a School of Life and Environmental Sciences, Faculty of Science, Engineering and Built Environment, Deakin University, Waurn Ponds, Victoria, 3216, Australia.

^b Centre for Regional and Rural Futures, Faculty of Science, Engineering and Built Environment, Deakin University, Waurn Ponds, Victoria, 3216, Australia.

^c Institute for Frontier Materials, Deakin University, Waurn Ponds, Victoria, 3216, Australia.

^d Current affiliation: School of Health and Life Sciences, Federation University, Mt Helen, Victoria, 3350, Australia.

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below the device. Further experimental details are included in the ESI.

Moon *et al.* reported a switch-on peak-to-peak square wave voltage (at 60 Hz) of 2.6 V_{pp} and luminance saturation at ~4 V_{pp} for an ECLD with [Ru(bpy)₃]Cl₂ luminophore.^{1a} Very little has been previously mentioned regarding the emission intensity over time in ionic gel-based ECLDs, but Hong *et al.*^{5a} showed that the emission of an ECLD prepared using P(VDF-HFP), [EMIM][TFSI] and [Ru(bpy)₃]Cl₂ (V_{pp} = 3 V, 1 Hz, operated continuously) decayed to half its initial intensity by ~4 min. A larger peak to peak voltage was required in our study, because of the greater viscosity of the ionic liquid.⁴ For the [Ru(bpy)₃](PF₆)₂ luminophore, we initially applied 5.0 V_{pp} at 60 Hz for 2 s, which we repeated with 3 s rest intervals (Fig. S2). Under these conditions, the emission appeared as a bright flash followed by a lower intensity glow, predominantly emanating from the edges of the silver electrode area. Moreover, the intensity of emission decayed rapidly over repeated pulse sequences using the same silver electrode (Fig. S3). To improve the lifetime of the emission, we examined the electrochemical properties of the luminophore in acetonitrile solution using a 3-electrode cell, and within the 2-electrode ECLD where the ITO served as both counter and reference (Table 1). These experiments showed that the peak-to-peak voltage could be minimised by applying a lower cathodic than anodic potential, whereas previously only equivalent magnitude potentials have been applied in ECLDs.

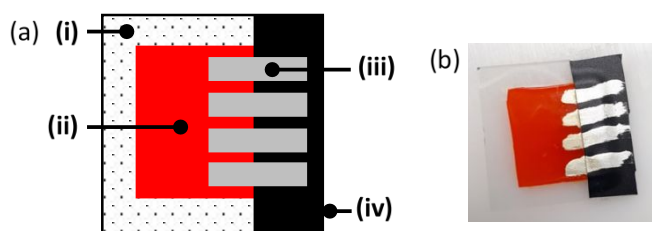


Fig. 1. (a) Schematic diagram of the ECLD, showing: (i) ITO electrode; (ii) gel layer (a mixture of luminophore, polymer (P(VDF CO HFP) dissolved in acetone) and ionic liquid ([BMIM][TFSI]) in a 1:4:16 mass ratio); (iii) silver conductive paint; and (iv) insulation tape. (b) Photograph of an ECLD containing the [Ru(bpy)₃](PF₆)₂ luminophore.

The effect on emission intensity and lifetime were examined by firstly varying the applied cathodic potential while holding the anodic potential at +2.5 V. Although the greatest intensity was obtained using -2.0 V (Fig. 2a), the least degradation of emission intensity, both over each 2 s pulse and between the second and third pulses, occurred using -1.0 V (Fig. S5). Comparison of the intensities when varying the anodic potential showed that at least +2.4 V was required (Fig. 2b) and based on the peak shapes (Fig. S6), +2.5 V was selected. Decreases in emission intensity and lifetime of the ECLD at high magnitude potentials can be ascribed to deleterious electrochemical reactions with the ionic gel matrix,^{5a, 5c} and further (irreversible) oxidations/reductions of the luminophore.^{9b, 10b} Using potentials of +2.5 and -1.0 V, the emission degraded to half its initial intensity after 272 pulses (23 min; Fig. 2c) compared to

only 12 pulses when +2.5 V and -2.5 V were applied (Fig. S3). When the ECLD was operated continuously (60 Hz; without rest times), the emission degraded to half its peak intensity over 18 min (Fig. S7).

Moon *et al.*^{1a} reported that the inclusion of a red ([Ru(bpy)₃]Cl₂) and green ([Ir(df-ppy)₂(bpy)](PF₆)) luminophore in an ECLD (at mole ratios from 20:80 to 80:20) resulted in emission only from the red emitter. Our investigations of ECL from mixtures of metal complexes in acetonitrile,⁹ however, show emission from both luminophores when more extreme ratios are used. We therefore examined the possibility of tuning the emission colour of ECLDs by adding relatively small amounts of the red emitter. Using the same approach as described for [Ru(bpy)₃](PF₆)₂, the most appropriate potentials for [Ir(df-ppy)₂(bpy)](PF₆) were found to be +2.5 V and -1.8 V. By incorporating the luminophores at mole ratios of 3:97 to 10:90 [Ru(bpy)₃](PF₆)₂:[Ir(df-ppy)₂(bpy)](PF₆), we obtained colours from green through yellow to orange (Fig. 3a), which could be characterised through the corresponding transition of RGB values (Fig. 3b) and an S-shaped curve on a CIE plot (Fig. 3c).

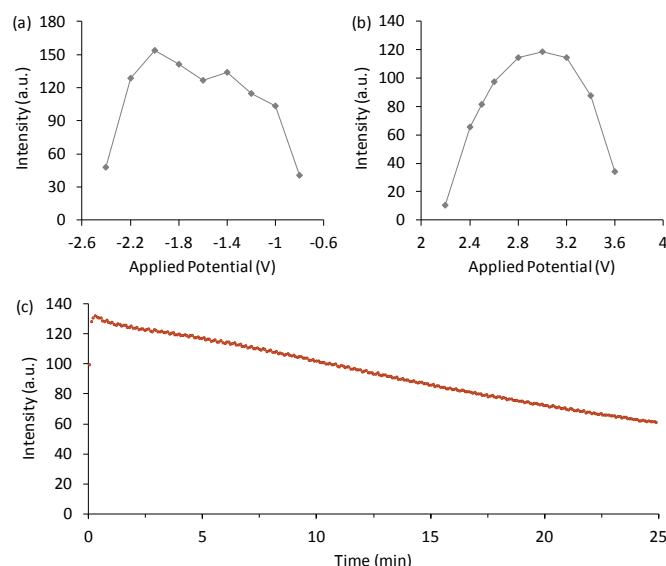


Fig. 2. (a) ECLD intensity upon application of different cathodic potentials with an anodic potential at 2.5 V (60 Hz). (b) ECLD intensity upon application of different anodic potentials with a cathodic potential at -1.0 V (60 Hz). (c) ECLD emission upon application of 300 square wave pulse sequences of 2 s, 60 Hz, +2.5 V and -1.0 V, with 3 s rest times, where each data point is the average ECL intensity over the 2 s pulse.

At a luminophore ratio of 60:40, Moon *et al.*^{1a} observed a two-fold enhancement in the red emission of [Ru(bpy)₃]Cl₂. Recently, Oh *et al.*⁷ reported a similar increase in intensity from [Ir(ppy)₂(bpy)](PF₆) when including [Ir(df-ppy)₂(bpy)](PF₆) at a ratio of 40:60. In both cases, the mechanism of enhancement was postulated^{1a, 7} to involve electron transfer between the electronically excited [Ir(df-ppy)₂(bpy)]^{+*} and the oxidised form of the lower energy luminophore (*e.g.*, Eqn 1).

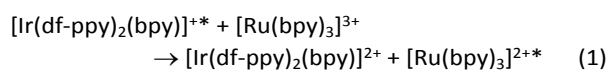


Table 1. Selected spectroscopic and electrochemical properties of the luminophores.

Luminophore	Photoluminescence ^a		Potentials (ACN solution) ^{a,b}					Potentials (ECLD) ^{a,c}		
	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{max}}/\text{eV}$	$E^{\text{O}^{\text{I}}(\text{ox})}/\text{V}^{\text{d}}$	$E^{\text{O}^{\text{I}}(\text{red})}/\text{V}^{\text{d}}$	ΔE	$E^{\text{O}^{\text{I}}(\text{M}^*/\text{M}^*)}/\sqrt{V^{\text{O}^{\text{I}}\text{b}, 9\text{c}, 11}}$	$E^{\text{O}^{\text{I}}(\text{M}^*/\text{M}^-)}/\sqrt{V^{\text{O}^{\text{I}}\text{b}, 9\text{c}, 11}}$	$E^{\text{O}^{\text{I}}(\text{ox})}/\text{V}^{\text{d}}$	$E_{\text{p}}(\text{red})/\text{V}^{\text{e}}$	ΔE
[Ru(bpy) ₃](PF ₆) ₂	622	1.99	+0.89	-1.73	2.62	-1.25	+0.40	+2.18	-0.94	3.12
[Ir(df-ppy) ₂ (bpy)](PF ₆)	525	2.36	+1.20	-1.72	2.92	-1.20	+0.74	+2.20	-1.41	3.61
[Ir(df-ppy-CF ₃) ₂ (ptb)](PF ₆)	470, 495	2.64	+1.35	-1.88	3.23	-1.35	+0.82	+2.48	-1.79	4.27

^aSpectra and cyclic voltammograms are shown in Fig. S4. ^bPotential vs Fc⁺/Fc⁰. ^cPotential vs CE. ^dFormal potentials. ^ePeak reduction potential.

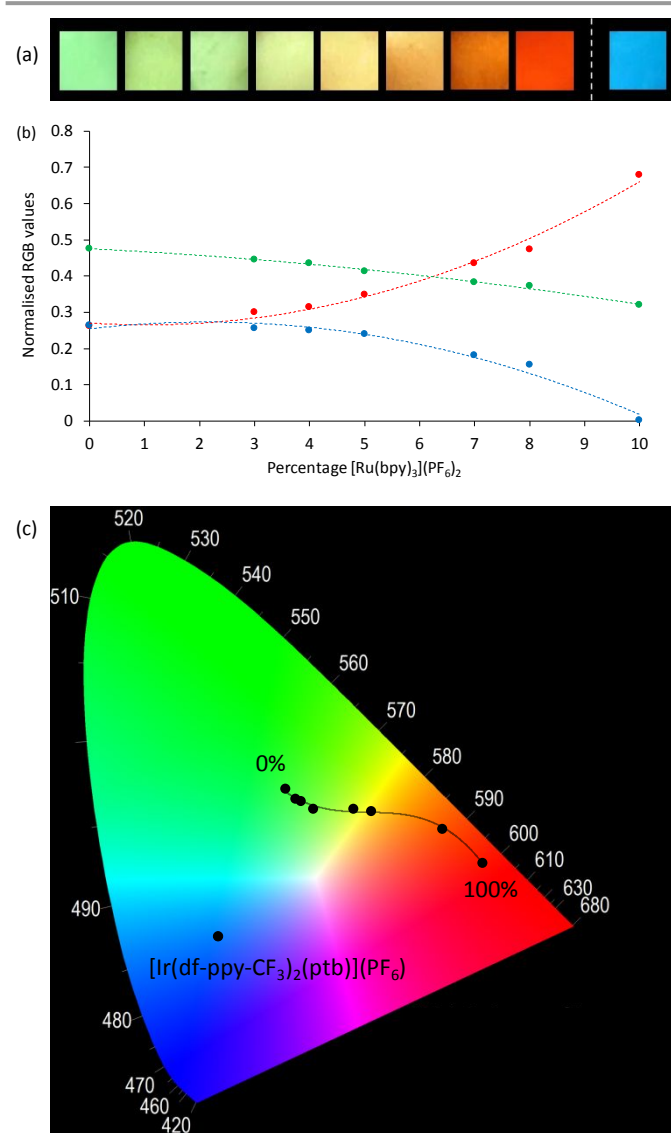
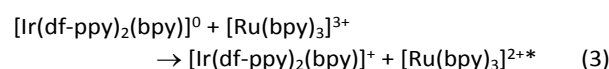
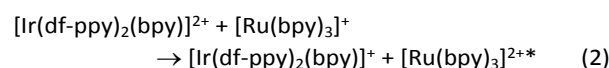


Fig. 3. (a) Photographs of emission from the ECLDs incorporating the red ([Ru(bpy)₃](PF₆)₂) and green ([Ir(df-ppy)₂(bpy)](PF₆)) luminophore in the mole ratio 0:100, 3:97, 4:96, 5:95, 7:93, 8:92, 10:90 and 100:0, upon application of potentials of +2.5 V and -1.8 V (60 Hz) or (rightmost image) the blue ([Ir(df-ppy-CF₃)₂(ptb)](PF₆)) luminophore, at potentials of +2.8 V and -2.2 V (60 Hz). (b) Normalised RGB values for the above images. (c) CIE plot of the emission colours.

Examination of the reduction potentials of the relevant ground/excited states and the excited state energies, however, suggests that this pathway may not be feasible for these metal complex pairs (Fig. S8).^{9b} Alternatively, the excited state of the lower energy luminophore may be populated by the 'mixed'

annihilation ECL reaction between the two systems (e.g., Eqn 2 or 3). These pathways can be implemented at lower peak-to-peak voltages than those required to initially excite the higher energy luminophore.



The [Ir(df-ppy)₂(bpy)](PF₆) complex has previously been used as green luminophore (in the absence of other metal complexes)^{1a, 4, 5d} or to enhance the emission from lower energy orange-red luminophores.^{1a, 7} With the above concepts in mind, we sought to instead combine it with a metal complex with higher energy excited state to enhance the intensity of its inherent green emission.

Metal complexes with higher energy emissive states than [Ir(df-ppy)₂(bpy)](PF₆) have not previously been utilised in ECLDs. We therefore selected the related blue luminescent [Ir(df-ppy-CF₃)₂(ptb)](PF₆) complex (Fig. S1c and S4; Table 1) as a possible higher energy emitter/donor. Examination of the ECLD response at different applied potentials showed that +2.8 V and between -2.0 V and -2.2 V were suitable.

The ECLD emission with this luminophore was a sky-blue colour (Fig. 3a, rightmost image) with CIE coordinates of 0.21 and 0.25. The intensity was lower than that of the green luminophore and decayed rapidly over the first few 2 s pulse sequences (Fig. S9a), presumably due to the lower reversibility of the redox species (Fig. S4) and/or the position of these couples within the potential window of the matrix.^{5a, 9c, 12} When combined with the green emitter, however, enhancement was observed at a lower peak-to-peak voltage than that established for the [Ir(df-ppy-CF₃)₂(ptb)](PF₆) complex. Using a 55:45 mole ratio [Ir(df-ppy)₂(bpy)](PF₆)/[Ir(df-ppy-CF₃)₂(ptb)](PF₆) and a pulse sequence with potentials of +2.5 V and -2.2 V, the green emission was enhanced by 48% over that of [Ir(df-ppy)₂(bpy)](PF₆) alone. As the applied oxidation potential is lower than that used to rapidly populate the excited state of the blue luminophore in the ECLD matrix, the enhancement can be ascribed to the greater efficiency of the mixed annihilation reaction between the reduced [Ir(df-ppy-CF₃)₂(ptb)]⁰ and oxidised [Ir(df-ppy)₂(bpy)]²⁺ species, compared to the annihilation ECL of [Ir(df-ppy)₂(bpy)]⁺ alone. Importantly, the enhanced green emission did not suffer the rapid decay in intensity (Fig. S9b) that was observed with the blue luminophore alone at greater peak-to-peak voltages.

The number of reported luminophores (and thus the options for emission colour) for ECLDs to date is quite limited, and the approach presented herein enables access to a wide range of colours using two already established ECLD luminophores, without the need to design and evaluate new metal complexes with suitable spectroscopic and electrochemical properties. Moreover, we have shown that the intensity from higher energy luminophores (*e.g.*, the green emission of $[\text{Ir}(\text{df-ppy})_2(\text{bpy})]^+$) can be enhanced by other species through electron transfer pathways that do not require energy transfer from another excited state. Throughout this investigation, dissimilar magnitude anodic and cathodic potentials were exploited as a new approach to minimise the peak-to-peak voltages and maximise the emission stability of the ECLDs.

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Conflicts of interest

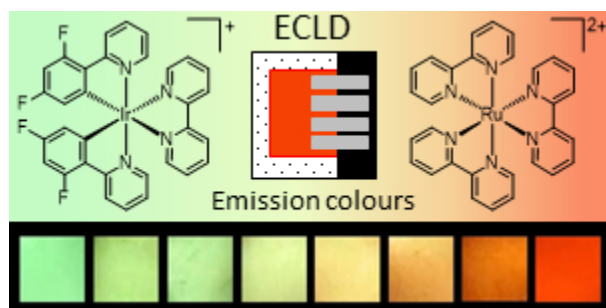
There are no conflicts to declare.

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Table of contents text (max 20 words):

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