**Electronic Supplementary Information** 

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

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## **Chemicals and materials**

Indium Tin Oxide (ITO) coated glass slides (25 mm × 25 mm; 8-12 ohm/cm resistivity), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][TFSI]) ionic liquid, poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF CO HFP)) polymer and the tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate ([Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>) luminophore were purchased from SigmaAldrich (Australia). Silver conductive paint was obtained from Electrolube (Australia) and acetone was purchased from Ajax Finechem (Australia). The [Ir(df-ppy-CF<sub>3</sub>)<sub>2</sub>(ptb)](PF<sub>6</sub>) and [Ir(df-ppy)<sub>2</sub>(bpy)](PF<sub>6</sub>) complexes were synthesised and characterised as previously described.<sup>1</sup>

## **Experimental details**

To prepare the ECLDs, the luminophore (Fig. S1), polymer (P(VDF CO HFP) dissolved in acetone) and [BMI][TFSI] ionic liquid were combined in a 1:4:16 mass ratio. The mixture was then vortexed and sonicated to dissolve the luminophore, then pipetted into a mould made of laser-cut silicon tape on ITO coated glass and left to set for 10 min. The silicon tape mould was removed and the device was heated in an oven (30°C, 24 h) and then stored overnight under vacuum in a desiccator. Insulation tape was then placed over a portion of the gel and ITO, and strips of silver paint were applied to form the upper electrodes.

An Autolab (Metrohm Autolab B.V., Netherlands) PGSTAT 128N potentiostat was used to conduct electrochemical experiments. A two-electrode set-up was used, with the working electrode (WE) connected to a painted silver electrode point. The counter electrode (CE) and reference electrode (RE) were both connected to the ITO. A two-step chronoamperometric sequence was applied at 60 Hz for 2 s and repeated two additional times with a three second rest period between each sequence (Figure S2). The cyclic voltammetry experiments shown in Figure S3 were conducted using a scan rate of  $0.1 \text{ V s}^{-1}$ . All experiments were connected in a light-tight faraday cage that housed the ECLD and camera.

The emission from the ECLD was recorded over time using a Canon EOS 6D camera (Canon, Japan), which was fitted with a Tonika AT-X PRO MACRO 100 mm f/2.8 D lens (Kenko Tonika, Japan). The camera was manually focused on the ITO base of the ECLD, which was positioned 15 cm above the lens. The camera operation was synchronised with the start and end of each electrochemical experiment using a simple relay and transistor switch that was controlled by the potentiostat *via* the DIO port. An ISO value of 6400 was used for all video and the f/ (aperture) value was adjusted to ensure the emitted light levels remained within an analysable range. Images in Fig. 3a have been enhanced (applying 1% shadow, 25 vibrance and 5 saturation in Adobe Photoshop) to highlight the differences in colour.

The videos were analysed using Tracker software (https://physlets.org/tracker/). The emission area of the ECLD was analysed using the 'RGB Region' feature to collect the mean Red, Green and Blue (RGB) channel values. The RGB values for each frame were then plotted over time as the video played in the software. The data was exported to Excel.



**Figure S1**. Luminophores: (a)  $[Ru(bpy)]^{2+}$ , (b)  $[Ir(df-ppy)_2(bpy)]^+$ , and (c)  $[Ir(df-ppy-CF_3)_2(ptb)]^+$ . In each case the counter ion was hexafluorophosphate.



**Figure S2.** (a) Example of the WE potential appied to the ECLD, and (b) magnification of a section of one applied pulse sequence showing the 60 Hz square wave.



**Figure S3**. Average intensity (a) overall and (b) in RGB channels of the second 2 s square wave pulse of each of a series of  $3 \times 2$  s pulse sequences (applying +2.5 V and -2.5 V at 60 Hz) for the ECLD with  $[Ru(bpy)_3](PF_6)_2$  luminophore. The broad red emission of the luminophore (Figure S3a) is predominantly recorded in the R channel, but gives a significant proportional response in the G channel. The G channel can therefore be used as a measure of intensity when the maximum response in the red channel is exceeded.



**Figure S4**. (a) Photoluminescence emission spectra, (b) cyclic voltammograms at a concentration of 0.2 mM in acetonitrile with 0.1 M TBAPF<sub>6</sub> in a conventional 3-electrode electrochemical cell, (c) cyclic voltammograms of the ECLD, for  $[Ru(bpy)]^{2+}$  (red lines),  $[Ir(df-ppy)_2(bpy)]^+$  (green lines), and  $[Ir(df-ppy-CF_3)_2(ptb)]^+$  (blue lines). All CVs were conducted using a scan rate of 0.1 V s<sup>-1</sup>.



**Figure S5**. Examples of the relative intensity of light emitted over the second and third 2 s pulse, with each pulse alternating (60 Hz) between +2.5 V and (a) -0.8 V, (b) -1.0 V, (c) -1.2 V, (d) -1.6 V, (e) -2.0 V, and (f) -2.2 V. The first pulse was excluded from this comparison as its shape was typically not representative of subsequent pulses.



**Figure S6**. Examples of the relative intensity of light emitted over the second and third 2 s pulse, with each pulse alternating (60 Hz) between -1.0 V and (a) 2.2 V, (b) 2.4 V, and (c) 2.5 V, (d) 2.8 V, (e) 3.2 V, (f) 3.6 V. The first pulse was excluded from this comparison as its shape was typically not representative of subsequent pulses.



**Figure S7**. ECLD emission (luminophore:  $[Ru(bpy)_3](PF_6)_2$ ) upon application of a continuous square wave function (60 Hz; +2.5 V and -1.0 V), with no rest periods.



**Figure S8**. Graphical depiction of the differences in ground and excited state reduction potentials for (a) the green luminophore  $[Ir(df-ppy)_2(bpy)]^+$  and red luminophore  $[Ru(bpy)_3]^{2+}$  (showing the redox couples involved in eqns 1-3) and (b) the blue luminophore  $[Ir(df-ppy-CF_3)_2(ptb)]^+$  and green luminophore  $[Ir(df-ppy)_2(bpy)]^+$ , in acetonitrile solution containing 0.1 M TBAPF<sub>6</sub>.



**Figure S9**. Examples of the intensity of light emitted over three 2 s pulses, for (a) the ECLD containing the blue [Ir(df-ppy-CF<sub>3</sub>)<sub>2</sub>(ptb)](PF<sub>6</sub>) luminophore with each pulse alternating (60 Hz) between +2.8 V and -2.2 V and (b) the ECLD containing a 50:50 ratio of the green [Ir(df-ppy)<sub>2</sub>(bpy)](PF<sub>6</sub>) luminophore and the blue [Ir(df-ppy-CF<sub>3</sub>)<sub>2</sub>(ptb)](PF<sub>6</sub>) luminophore with each pulse alternating (60 Hz) between +2.5 V and -2.2 V.

## References

- 1. E. Kerr, E. H. Doeven, G. J. Barbante, C. F. Hogan, D. J. Hayne, P. S. Donnelly and P. S. Francis, *Chem. Sci.*, 2016, **7**, 5271-5279;
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