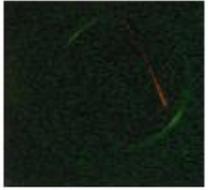
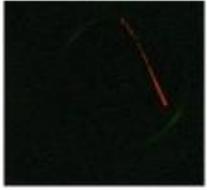
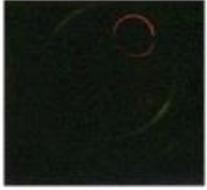


Electronic Supplementary Information

'Cathodic' Electrochemiluminescence of $[\text{Ru}(\text{bpy})_3]^{2+}$ and Tri-*n*-propylamine Confirmed as Emission at the Counter Electrode

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Table S1: Potentials (vs Ag/AgCl) applied at the working electrode and measured at the Pt wire counter electrode. The photographs were recorded on an EOS 6D DSLR camera (Canon, Japan) fitted with a Tonika AT-X PRO MACRO 100 mm f/2.8 D lens (Kenko Tonika, Japan). A 40 s exposure time was utilised for each image with an ISO value of 8000 and an aperture of F2.8. Conditions: 0.1 M phosphate buffer solution containing 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 50 mM TPrA (pH = 6.8). The lower images show the experiment repeated with the Pt wire electrode shaped into a ring.

Applied potential (V)	-1.20	-1.30	-1.40	-1.50
				
Counter potential (V)	0.83	0.85	0.88	0.93
				
Counter potential (V)	0.80	0.83	0.86	0.93

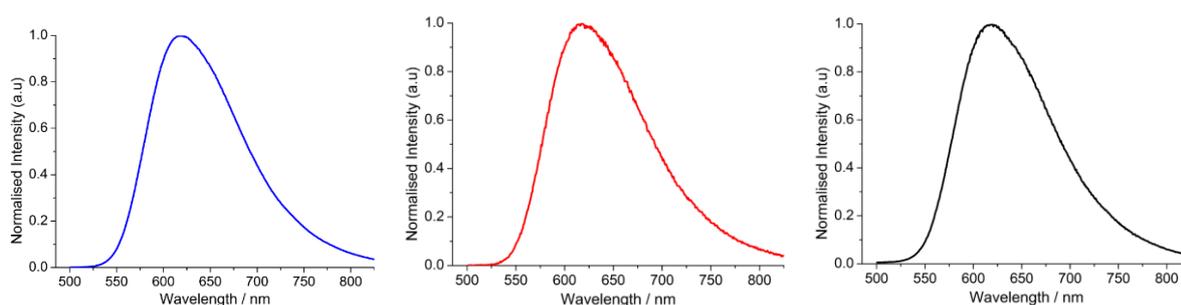


Fig. S1: Emission spectra for ECL at the counter electrode (blue line) upon application of cathodic potentials at the working electrode, as shown in Fig. 1; and ECL at the working electrode (red line) upon application of anodic potentials, as shown in Fig. 2, for 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ with 50 mM TPrA in 0.1 M phosphate buffer (pH = 6.8) solution; and the photoluminescence (black line) for the same solution upon excitation with UV light (370 nm LED).

Experimental details

All cyclic voltammetry experiments were conducted using an Autolab PGSTA12 potentiostat (Metrohm Autolab B.V, Netherlands) and chronoamperometry using an Autolab PGSTAT128N potentiostat (Metrohm Autolab B.V). The electrochemical cell comprised a cylindrical glass vessel with a flat base and custom-built Teflon lid with appropriately sized holes to fit the relevant electrodes. A 3 mm glassy carbon working electrode (CH instruments), leak free Ag/AgCl reference electrode (model KZT-5, 5 mm diameter; Innovative Instruments, USA) and either a 2 mm platinum disk or platinum wire counter electrode was utilised for all experiments. The potentiostat was outfitted with a pX1000 module configured to measure the potential difference between the counter and reference electrode, alongside measurement of the current and the applied working electrode potential. Prior to each experiment, each electrode was cleaned/polished. Glassy carbon and platinum disk electrodes were polished using 0.05 mm alumina powder on a felt pad with deionised water. All electrodes were rinsed with acetone and dried with either nitrogen or argon. For all experiments, the electrochemical cell was housed in a custom-built light-tight faraday cage.

ECL emission was monitored with an extended-range trialkali S20 photomultiplier tube (PMT; ET Enterprises model 9828B) positioned under the cell. Alternatively, the ECL at the working and counter electrodes was photographed using a Canon EOS 6D DSLR camera (Canon, Japan) fitted with a Tonika AT-X PRO MACRO 100 mm f/2.8 D lens (Kenko Tonika Co., Japan), which was interfaced with and controlled by the potentiostat. The camera was positioned directly under the base of the electrochemical cell (within the light tight faraday cage) and focused manually on the surface of the electrodes. An ISO value of 8000 and aperture of F2.8 was used for all images. To collect emission spectra, we replaced the camera with an Ocean Optics QEPro CCD spectrometer interfaced with the cell *via* optical fibre (1.0 m length, 1.0 mm core diameter) and collimating lens (Ocean Optics 74-UV).