Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Multi-colour bipolar electrochemiluminescence for heavy metal ion detection

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1.1 Chemicals

Tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate 97%, tris[2-phenylpyridinato-C2,N]iridium(III) 99%, tri-n-propylamine (TPrA) 98% and tetrabutylammonium hexafluorophosphate 98% ($TBAPF_6$) were purchased from Sigma Aldrich. Acetonitrile (ACN, HPLC grade) was purchased from Honeywell and distilled for 4 hours over nitrogen CaH_2 to remove any impurities. 0.01 M phosphate buffer pH 5 solution (PBS) was prepared by mixing potassium dihydrogen phosphate (98% Sigma Aldrich) and potassium hydrogen phosphate (99% Riedel de haen) solutions. All other chemical reagents were analytical grade and used without any purifications. Aqueous solutions were prepared in Millipore water (18.2 MΩ.cm).

1.2 Instrumentation

Electrochemical experiments were performed with either a PGSTAT12 AUTOLAB electrochemical potentiostat (MEP Instruments, NorthRyde, NSW, Australia) with NOVA 2.1 software or a CHI420A potentiostat (CH Instruments, Austin, Texas, USA). Electrochemical characterizations were performed in three-electrode mode consisting of a 3 mm diameter glassy carbon disc working electrode shrouded in Teflon (CH Instruments, Austin, Texas, USA), platinum wire (flame cleaned) as the counter electrode and silver wire as the quasi-reference electrode. ECL was detected by a Nanolog CCD (HORIBA Jobin Yvon IBH) spectrometer, Ocean optics QEPro spectrometer and a photomultiplier tube (PMT) module (Sens-Tech model P30A-05, ETP, NSW, Australia). The PMT signal was amplified by TA-GI-74 Ames Photonics Inc. amplifier (Model D7280).

1.3 BPE design

Sensing reservoir (Figure S 1) 200 µL aqueous samples were pipetted on the electrodes of a 3 mm diameter carbon paste screen printed electrode (Zensor R&D, Taiwan).

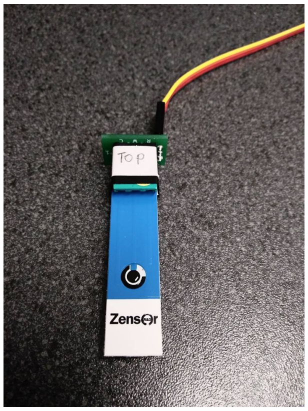

Figure S1. Sensing reservoir of closed BPE-ECL setup: carbon paste screen electrode

Reporting reservoir (Figure S2) The reporting reservoir stage was designed in SketchUp (Trimble Inc) and 3D-printed (DREAMER 3D PRINTER, FlashForge) in two components: an optical fibre component as seen in Figure S2a and electrode component (Figure S2b). The electrode component includes a 4.3×12 mm (diameter × depth) hole designed to fit both around the glassy carbon disc electrode and plastic sleeve used to hold the sample. Four 3×4 mm neodymium magnets were glued into each corner of the component, as well as the fibre optic component so that the two connected magnetically. The optical fibre component includes an 8×12 mm hole in which the fibre optic fit securely. 250 µL reporter solutions containing 1 mM $Ir(ppy)_3$, 0.05 mM $Ru(bpy)_3(PF_6)_2$, 10 mM TrPA and 0.1 M $TBAPF_6$ in ACN were added above the electrode in the plastic sleeve. (Note that these optimal concentrations for BPECL differ slightly from the concentrations used for the conventional 3-electrode ECL experiments in Figure 2). Between the two components was a thin (1 mm diameter) Pt wire which acts as a driving electrode (Figure 1, main text). A power supply was connected to the Pt wire and the SPE's auxiliary electrode. A copper wire connected the glassy carbon electrode and the working electrode of the SPE to establish the connection between the bipolar electrodes. The optical fibre connected the reporting reservoir and the light detector (PMT or Ocean Optics CCD camera).

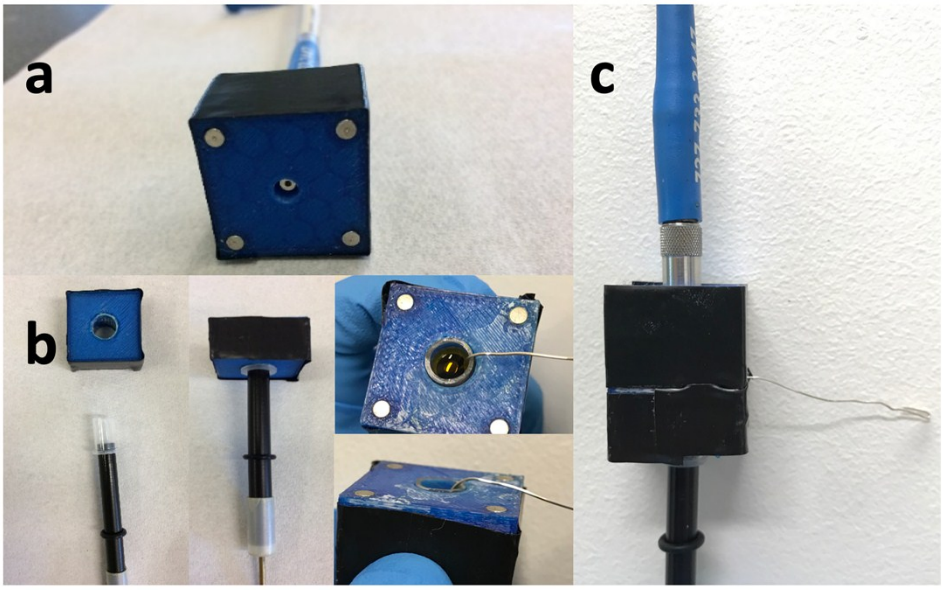

Figure S2. Reporting reservoir of closed BPE-ECL setup: optical fiber component **(a)**, glassy carbon and pt wire electrodes component **(b)** and the whole reporting reservoir **(c)**. Eight neodymium magnets connected the two components.

1.4 ECL mechanism

The co-reactant forms a highly reducing radical species that is capable of transferring an electron to the oxidized luminphore to produce an excited state, as outlined for the case of $Ir(ppy)_3$ in equations 1-4.

$$\mathbf{Ir(ppy)_3 - e^- \rightarrow Ir(ppy)_3^+} \quad \textbf{(1)}$$

$$\mathbf{TPrA - e^{-} \rightarrow [TPrA^{\bullet}]^{+} \rightarrow TPrA^{\bullet} + H^{+}} \tag{2}$$

$$\mathbf{Ir(ppy)_3^{+} + TPrA^{\bullet} \rightarrow Ir(ppy)_3^{*} + Products} \tag{3}$$

$$\mathbf{Ir(ppy)_3^{*} \rightarrow Ir(ppy)_3 + \mathit{hv}} \tag{4}$$

1.5 3D BPE-ECL procedure

BPE-ECL measurements were performed by scanning the potential at the driver electrode while the CCD camera simultaneously detected the optical readout. This was to understand better the BPE-ECL emission in the presence of target metal ions in the sensing reservoir. To synchronize the CCD camera and potentiostat, a triggering pulse from the PGSTAT was sent to the Ocean Optics, which started the measurement. The scan rate of the potential at the driving electrode was 20 mV.s^{-1} and the CCD integration time was 2 s.

1.6 Supporting Figures

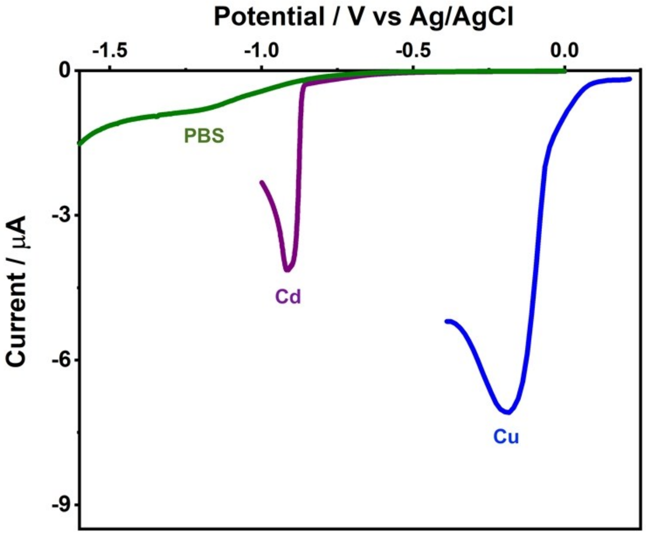

Figure S3. LSV of PBS solution (0.1 M, pH=7.4) (green trace), 100 µM Cd^{2+} in PBS solution (violet trace), 100 µM Cu^{2+} in PBS solution (blue trace).

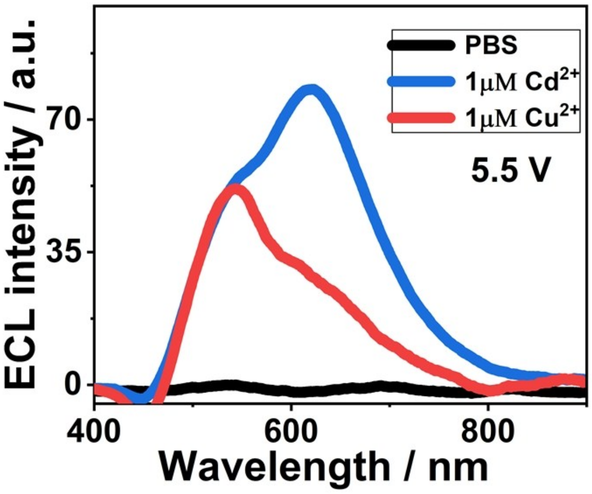

Figure S4. Difference between BPE-ECL colour emissions at 5.5 V of a mixture of 1 mM Ir(ppy)$_3$, 0.1 mM Ru(bpy)$_3^{2+}$, 15 mM TPrA and 0.1 M TBAPF$_6$ in acetonitrile in the reporting reservoir, while in the sensing reservoir PBS (black trace), PBS / 1 µM Cd^{2+} (red trace), PBS / 1µM Cd^{2+} (blue trace).

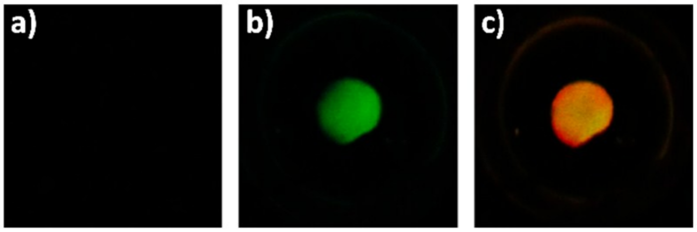

Figure S5. Photos of GC electrode surface for **a)** PBS, **b)** Cd^{2+} 1 µM and **c)** Cu^{2+} 1 µM at 5.5 V. The photo has been taken with 10 s exposure time.