

Electrochemically, Spectrally, and Spatially Resolved Annihilation-Electrogenerated Chemiluminescence of Mixed-Metal Complexes at Working and Counter Electrodes

Lachlan C. Soulsby,^[a] David J. Hayne,^[a] Egan H. Doeven,^[b] Lifan Chen,^[a] Conor F. Hogan,^[c] Emily Kerr,^[a, d] Jacqui L. Adcock,^[a] and Paul S. Francis^{*[a]}

Previously dismissed as an unwanted and unpredictable artifact of electrogenerated chemiluminescence (ECL) systems, emission at the counter electrode has new importance in the context of the emerging multicolor and potential-resolved ECL systems in which a much wider range of potentials are applied at the working electrode. Herein, we explore the annihilation ECL from a mixture of two electrochemiluminophores at both the working and counter electrodes of a three-electrode electrochemical cell. The potentials at the working and counter electrodes were both measured, and the simultaneous spatially resolved ECL was captured with a digital camera. The factors that determine the dominant emitter (and therefore the observed emission color) at the working electrode can be applied to the counter, albeit with a less well-defined potential range. A variety of color combinations from the luminophores can be elicited at the two electrode surfaces through the selection of applied potentials.

Recent exploration of co-reactant and annihilation electrogenerated chemiluminescence (ECL) from mixtures of metal-complex luminophores has revealed new opportunities to develop multiplexed detection systems and simple multicolored light emitting devices.^[3] In 2012 we showed that the ECL of multiple metal complexes in solution (such as $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\lambda_{\text{max}} = 621 \text{ nm}$; Table 1) and *fac*- $\text{Ir}(\text{ppy})_3$ ($\lambda_{\text{max}} = 520 \text{ nm}$) with tri-*n*-propylamine (TPrA) as a co-reactant) could be resolved by

both the spectral distribution of their emission and the distinct oxidation potentials required for their excitation.^[4] Moreover, not only could the luminophores be 'switched on' at different applied potentials, but in some cases they were also 'switched off' at high overpotentials, through an unanticipated oxidative quenching of the excited state by TPrA^{•+}.^[5] These concepts were subsequently expanded by our group and others through demonstrations of electrochemically tunable multicolored ECL from a single Ir(III) complex^[6] and heterodinuclear Ru(II)/Ir(III) complexes,^[7] and most recently, ECL from multiple metal complexes within 'bipolar electrochemistry' systems.^[8]

In general, bipolar electrochemistry describes the application of an electric field to an electrolyte solution containing one or more conducting objects, to induce anodic and cathodic poles in the object(s), at which electrochemical reactions can be performed.^[9] Bipolar electrochemistry has been utilized to initiate ECL,^[10] and adapted to simultaneously initiate two distinct ECL systems that emit different colored light, either where both reactions were initiated at the anodic end of multiple bipolar objects in spatially resolved zones (e.g., orange-red light from $[\text{Ru}(\text{bpy})_3]^{2+}$ with various co-reactants, and blue light from luminol with H_2O_2),^[11] or where one reaction is triggered by oxidation ($[\text{Ru}(\text{bpy})_3]^{2+}$ and TPrA) and the other by reduction ($\text{Au@g-C}_3\text{N}_4$ nanocomposites and O_2) at the two ends of the bipolar objects.^[12]

In addition, Li et al. showed that the gradients of polarization potential across a bipolar object can be exploited for a spatially resolved 'snapshot' of the potential-resolved multicolor ECL from two metal complexes ($[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{Ir}(\text{ppy})_3$) in solution with TPrA.^[8a] Wang et al. utilized the potential-dependent multicolor emission from $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{Ir}(\text{ppy})_3$ (with TPrA) at the anodic end of a closed bipolar electrode as a visual

[a] L. C. Soulsby, Dr. D. J. Hayne, L. Chen, Dr. E. Kerr, Dr. J. L. Adcock, Prof. P. S. Francis
School of Life and Environmental Sciences, Faculty of Science,
Engineering and Built Environment,
Deakin University
Geelong, Victoria 3220, Australia
E-mail: paul.francis@deakin.edu.au

[b] Dr. E. H. Doeven
Centre for Regional and Rural Futures, Faculty of Science, Engineering and
Built Environment,
Deakin University
Geelong, Victoria 3220, Australia

[c] Prof. C. F. Hogan
Department of Chemistry and Physics, La Trobe Institute for Molecular
Science,
La Trobe University
Melbourne, Victoria 3086, Australia

[d] Dr. E. Kerr
Current affiliation: Monash Institute of Pharmaceutical Sciences, Monash
University
Parkville, Victoria 3052, Australia

Table 1. Selected spectroscopic and electrochemical properties of the two electrochemiluminophores.^[1]

Sample	$[\text{Ru}(\text{bpy})_3]^{2+}$	<i>fac</i> - $\text{Ir}(\text{ppy})_3$
PL (r.t.), λ_{max} [nm] ^[a]	621	520
PL (77 K), λ_{max} [nm] ^[a]	580, 628	494, 532
E_{0-0} [eV]	2.14	2.51
E_{ox}^0 [V vs. $\text{Fc}^{0/+}$]	0.89	0.33
E_{red}^0 [V vs. $\text{Fc}^{0/+}$]	−1.73, −1.92, −2.16	−2.67
ΔE [V]	2.62	3.00

[a] Corrected for the instrument sensitivity across the wavelength range.^[2]

reporter for a bioassay that modulated the resistance of the polar electrode.^[8b] Of course, bipolar-electrode ECL^[8,12] is not the only example in which simultaneous anodic and cathodic ECL has been observed; ECL at the surface of both the working and counter electrodes in conventional electrochemical cells has occasionally been reported, albeit as an unwanted interference.^[13] We have also noted annihilation ECL emission at the surface of both the working and counter electrodes within standard three-electrode cells.^[14]

In mixed annihilation ECL systems, the multiple potentials of the metal complexes offer effective electrochemical control of the system.^[14–15] We previously investigated the annihilation ECL of $[\text{Ru}(\text{bpy})_3]^{2+}$ and various $\text{Ir}(\text{III})$ complexes, and under suitable conditions, observed emission from one or both luminophores, which can be controlled by the applied potentials (Figure 1).^[14,15c] Simple estimations of the exergonic-

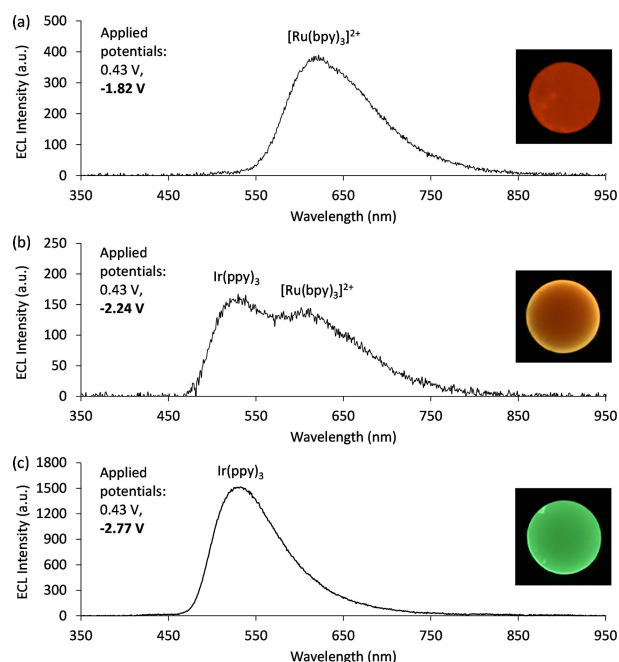


Figure 1. ECL spectrum and photograph of the emission from a mixture of 0.25 mM $\text{Ir}(\text{ppy})_3$ and 0.003 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile with 0.1 M TBAPF₆ supporting electrolyte, upon the application of three different sets of electrode potentials. Adapted from Ref. [14] (Copyright by The Royal Society of Chemistry).

ity of the reactions between the oxidized and reduced species under any set of applied potentials provided an effective prediction of which excited states could be attained (Note S(a) in the Supporting Information). The possibility of simultaneous, spatially resolved multicolor ECL at the counter electrode, however, is yet to be examined.

Herein, we explore the multicolor annihilation ECL from a mixture of two luminophores at both the working and counter electrodes of a conventional three-electrode system. We chose to use mixtures of $\text{Ir}(\text{ppy})_3$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ because these metal complexes (and various closely related species) are the most commonly used and well characterized for multicolored

ECL in both annihilation^[14,15c] and co-reactant^[4–5,8,16] modes of operation. To examine the simultaneous ECL processes occurring at the two electrodes, we added a differential electrometer to also measure the potential between the reference and counter electrodes (Figure S1), and a camera to record the spatially resolved emissions. We used identical glassy carbon electrodes as the working and counter electrodes (with Ag/AgCl reference). This provided a more reproducible cell configuration and the equal surface area promoted ECL at the counter electrode. In other electrochemical experiments, interference from uncontrolled reactions at the counter electrode can be minimized by isolating this electrode in a separate chamber from the working electrode chamber, between which the charge can be carried (through a glass frit for example). This is not suitable for ECL experiments, because it reduces potentiostatic control of the working electrode in the early stages of each applied pulse,^[17] when the current flow and ECL intensities are greatest. With the working and counter electrodes in the same chamber, undesirable reactions at the counter electrode can be minimized by ensuring that the surface area of the counter electrode is considerably larger than that of the working electrode.^[17] Depending on the application, this may require some compromise, as the ECL intensity is dependent in part on the surface area of the working electrode. Nevertheless, we have previously observed ECL from both working and counter electrodes on occasions under the typical experimental conditions utilized for ECL experiments (using, for example, a glassy carbon working electrode, platinum wire counter electrode and Ag/AgNO_3 reference electrode^[14]).

A higher concentration of $\text{Ir}(\text{ppy})_3$ than $[\text{Ru}(\text{bpy})_3]^{2+}$ was employed to compensate for the quenching of $\text{Ir}(\text{ppy})_3$ ECL in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$.^[15c] A mixture of 0.2 mM $\text{Ir}(\text{ppy})_3$ and 6 μM $[\text{Ru}(\text{bpy})_3]^{2+}$ enabled us to photograph the emissions at the working and counter electrodes across all experiments under the same two-step electrochemical pulse frequency and time (0.5 Hz for 12 s), changing only the applied potentials and the camera aperture. Figure 2a shows the potentials applied (black dots) in four experiments that generated different emissions at the working and counter electrodes (Figure 3).

The range for each counter electrode potential shown in Figure 2a (blue lines) arises from the change in potential during each pulse and between the six pulses of each experiment (e.g., Figure 4b), and not from changes between repetitions of the same experiment, which were generally quite consistent (e.g., Figure S2). The counter electrode potential shifts in response to growing or diminishing current at the working electrode, and therefore the counter electrode potential during the first pulses of the series were generally different from the later pulses (Figure 4b), due to the change in current between pulses. This increased the counter electrode potential ranges measured over each experiment.

In experiment 1 (Expt. 1), we applied a two-step potential pulse at the working electrode, comprising 1.03 V (vs. $\text{Fc}^{0/+}$), which was sufficient to oxidize both complexes, and -2.12 V, which reached the second reduction of $[\text{Ru}(\text{bpy})_3]^{2+}$. Reactions between these oxidized and reduced species provide sufficient energy to attain the excited state $[\text{Ru}(\text{bpy})_3]^{2+*}$, but not

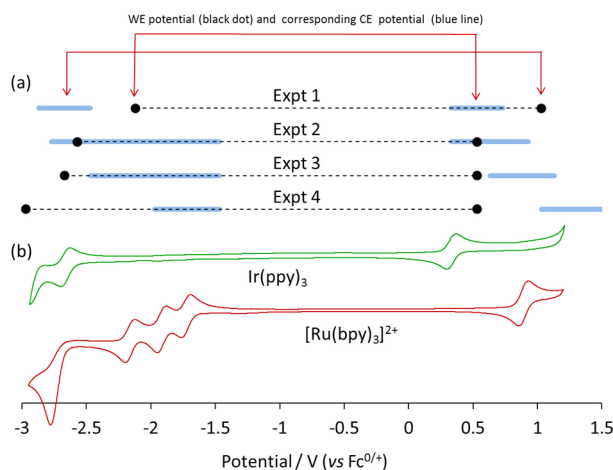


Figure 2. (a) The alternating two-step potential (0.5 Hz for 12 s) applied at the working electrode (black dots) and potential ranges measured at the counter electrode (blue lines), for four sets of experiments, using 0.2 mM Ir(ppy)₃ and 6 μM [Ru(bpy)₃]²⁺ in acetonitrile with 0.1 M TBAPF₆. (b) Cyclic voltammograms of Ir(ppy)₃ and [Ru(bpy)₃]²⁺.

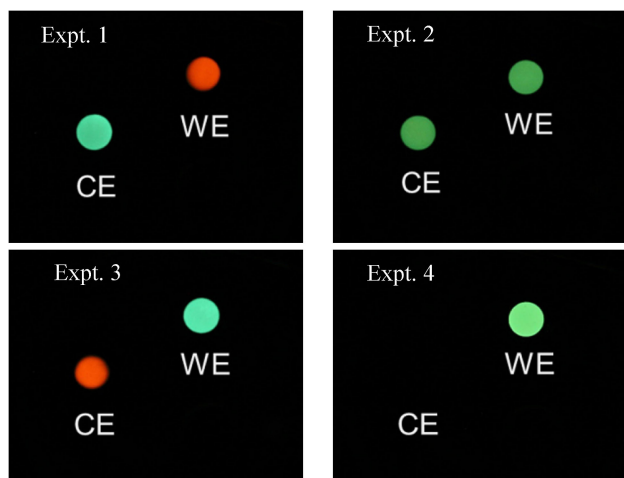
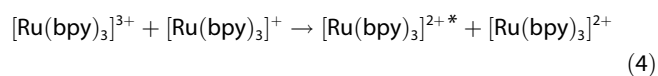
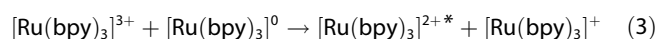
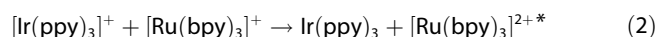
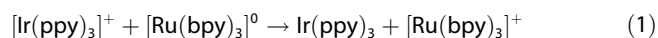


Figure 3. Photographs of the light emitted from the working electrode (WE) and counter electrode (CE) during the four experiments depicted in Figure 2. Conditions: camera ISO 8000, aperture (f-number) 4 (Expt. 1 and 2), 3.5 (Expt. 3), and 11 (Expt. 4).

Ir(ppy)₃* (Equations 1–4).^[14,15c] As anticipated, the characteristic orange-red emission of the [Ru(bpy)₃]^{2+*} was observed at the working electrode.



In the three-electrode system, the counter electrode voltage is varied to set and maintain each potential at the working electrode. To apply this two-step potential (−2.12 V and 1.03 V)

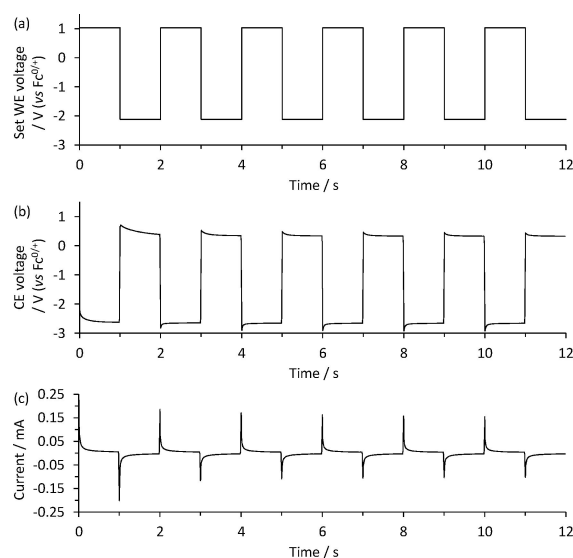
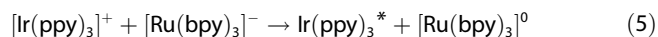


Figure 4. (a) Potential at working electrode, (b) potential at counter electrode, and (c) cell current, during Expt. 1 (as depicted in Figure 2). The potentials and current for Expt. 2–4 are shown in Figure S5–S7. Conditions: 0.2 mM Ir(ppy)₃ and 6 μM [Ru(bpy)₃]²⁺ in acetonitrile with 0.1 M TBAPF₆; electrodes: glassy carbon working and counter, Ag/AgCl reference; two-step potential pulse applied at 0.5 Hz for 12 s.

at the working electrode under our configuration, the voltage at the counter electrode varied from approximately 0.33 V to 0.73 V and from −2.87 V to −2.47 V, respectively. The 0.33 V to 0.73 V range is sufficient to oxidize Ir(ppy)₃, but not [Ru(bpy)₃]²⁺ and −2.87 V to −2.47 V will reduce both Ir(ppy)₃ and [Ru(bpy)₃]²⁺ (through four 1e[−] reduction steps). Unlike the species generated at the working electrode, those generated at the counter electrode are capable of forming Ir(ppy)₃* (Equations 5 and 6). The [Ru(bpy)₃]^{2+*} emitter can also be formed (Equation 2), but due to its partial inhibition by the irreversible fourth reduction of the ruthenium complex,^[15c] and the higher concentration of Ir(ppy)₃ than [Ru(bpy)₃]²⁺ in solution, the light emanating from the counter electrode under these conditions is predominantly the characteristic green luminescence from Ir(ppy)₃* (Figure 3, Expt. 1).



In Expts. 2–4, we applied a two-step potential pulse, comprising 0.53 V (capable of oxidizing Ir(ppy)₃, but not [Ru(bpy)₃]²⁺), and three different reductive potentials: −2.57 V, −2.67 V and −2.97 V, which in each case was sufficient to produce a green emission from Ir(ppy)₃* at the working electrode (Figure 3, Expt. 2–4). As described above, [Ru(bpy)₃]^{2+*} can also be formed, but it was not a major contributor to the observed emission under these conditions. The negative potential applied at the working electrode in Expt. 2 (−2.57 V) was sufficient reach the third reduction of [Ru(bpy)₃]²⁺ and therefore Ir(ppy)₃* was generated from Equation 5. At the counter electrode, the oxidative potential was sufficient to oxidize Ir(ppy)₃. The reductive potential covered a

wide range, which extended to potentials sufficient to reduce Ir(ppy)_3 . In this case, the green emission from Ir(ppy)_3^* was observed at both the working and counter electrodes (Figure 3, Expt. 2).

Expt. 3 differed from Expt. 2 by a small increase in the magnitude of the applied reduction potential to reach the $\text{Ir(ppy)}_3^{-/0}$ couple ($E_{\text{red}} = -2.67 \text{ V vs. Fc}^{0/+}$). The positive potentials measured at the counter electrode were greater and now included the $[\text{Ru(bpy)}_3]^{3+/2+}$ couple, and the negative potential range contracted so that it no longer included the $\text{Ir(ppy)}_3^{-/0}$ couple. Although the potentials at the counter electrode were sufficiently negative for a portion of the reductive pulses to reach the third reduction of $[\text{Ru(bpy)}_3]^{2+}$ (at which time Ir(ppy)_3^* could be formed from Equation 5), the emission observed at the counter electrode in Expt. 3 was predominantly the red-orange luminescence from $[\text{Ru(bpy)}_3]^{2+*}$ (Equations 2–4), in contrast to the green emission at the working electrode (Figure 3, Expt. 3).

In Expt. 4, we shifted the reductive potential at the working electrode further negative, which moved the corresponding voltage at the counter electrode further positive, extending it into the region where an additional oxidation process was observed for Ir(ppy)_3 (Figure S3). Under these conditions, the ECL at the counter electrode was quenched and only the green emission at the working electrode was observed (Figure 3, Expt. 4) (Note S(b), Supporting Information).

These experiments provide a new understanding of the concurrent ECL processes at the working and counter electrodes. This is particularly important considering the emergence of multicolor and/or potential-resolved ECL systems, which are inherently more vulnerable to this phenomenon. For annihilation ECL involving a single electrochemiluminophore in a typical three-electrode cell, potentials slightly beyond those required to oxidize and reduce that species are applied at the working electrode. Providing the active surface area of the counter electrode is large (and the resistance of the cell is low), the corresponding potentials at the counter electrode will generally be insufficient to generate the emitter.^[17] In contrast, for annihilation ECL involving multiple luminophores, the application of different potentials at the working electrode can be exploited to manipulate the ratio of emitters.^[14,15c] But these potentials can be much greater than those required to generate the lowest energy emitter. In the mixed annihilation ECL system of Ir(ppy)_3 and $[\text{Ru(bpy)}_3]^{2+}$, for example, the oxidation and reduction of Ir(ppy)_3 to generate Ir(ppy)_3^* (Equation 8) requires the application of potentials that differ by at least 3.00 V, whereas the generation of $[\text{Ru(bpy)}_3]^{2+*}$ from the oxidation of Ir(ppy)_3 and reduction of $[\text{Ru(bpy)}_3]^{2+}$ (Equation 4) requires potentials that differ by only $\sim 2.05 \text{ V}$. The difference in active surface areas may therefore be insufficient to keep the potentials required at the counter electrode below these minima. The chemistry of these mixed ECL systems may be in part the reason why we only recently had begun to observe light from the counter electrode in these systems, after many years of working with ECL reactions containing a single electrochemiluminophore, but perhaps more importantly, these systems have demanded new instrumental approaches, in

which the spectral distributions are recorded or the light emanating from the electrode surfaces is observed visually or photographed.^[5b,8,14,15c,18] Under these instrumental conditions, the spatially resolved emissions at different electrodes are immediately apparent.

Experimental Section

Chemicals

Reagents and solvents were purchased from various commercial sources and used without further purification. $\text{Tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate}$ ($[\text{Ru(bpy)}_3](\text{PF}_6)_2$) and tetrabutylammonium hexafluorophosphate (TBAPF_6 ; electrochemical grade) were purchased from Sigma-Aldrich (NSW, Australia). Bis(cyclopentadienyl)iron (ferrocene) was purchased from Strem Chemicals (MA, USA). *fac*- $\text{Tris(2-phenylpyridine)iridium(III)}$ (Ir(ppy)_3) was from Rubipy Scientific (ON, Canada). Potassium chloride for reference electrode storage was obtained from Labserv Pronalys (Vic., Australia). Acetonitrile was from Scharlau (Barcelona, Spain) and was distilled over calcium hydride under a nitrogen atmosphere and collected as needed. Solutions were degassed using argon or nitrogen for approximately 15 minutes prior to analysis.

Electrochemistry and ECL

Experiments were conducted using an Autolab PGSTAT128N potentiostat (Metrohm Autolab B.V., Netherlands). The electrochemical cell comprised a cylindrical glass vessel with a flat base and custom-built Teflon lid with appropriate sized holes to fit the relevant electrodes, ensuring a consistent electrode geometric configuration over time. Freshly distilled acetonitrile with 0.1 M TBAPF_6 supporting electrolyte was used as the solvent. Prior to each experiment, each electrode was cleaned/polished, and the solvent was degassed with either nitrogen or argon for 15 minutes. Glassy carbon electrodes were polished using 0.3 mm and 0.05 mm alumina powder on a felt pad with deionized water. All electrodes were rinsed with acetonitrile or acetone and dried with either nitrogen or argon. For ECL experiments, the electrochemical cell was housed in a custom-built light-tight faraday cage.

Cyclic voltammograms were collected using a glassy carbon working electrode (CH instruments), platinum wire counter electrode and silver wire reference electrode. Oxidation and reduction potentials were referenced, in situ, to the formal potential of the ferrocene/ferrocenium ($\text{Fc}^{0/+}$) couple (0.2 mM). For the examination of ECL at the working and counter electrodes, the three-electrode configuration comprised identical glassy carbon electrodes (3 mm diameter) as the working and counter electrodes, and a Ag/AgCl reference electrode (model KZT-5, 5 mm diameter; Innovative Instruments, USA). The potentiostat was outfitted with a pX1000 module. This module is normally used to measure the potential of a pH electrode while taking electrochemical measurements, but here the pX1000 was configured to measure the potential difference between the counter and reference electrode, alongside measurement of the current and the applied working electrode potential. 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 as previously described.^[5b] 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 was used for all images and the

aperture was adjusted as required. Images were analyzed using ImageJ software (<http://rsbweb.nih.gov/ij/>).

Acknowledgements

This work was funded by the Australian Research Council (DP160103046). E.K. was supported by an Australian Postgraduate Award Scholarship. L.C.S. and L.C. were supported by Deakin University Postgraduate Scholarships.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: counter electrode • iridium • luminescence • multicolor • potential-resolved

- [1] L. Chen, E. H. Doeven, D. J. D. Wilson, E. Kerr, D. J. Hayne, C. F. Hogan, W. Yang, T. T. Pham, P. S. Francis, *ChemElectroChem* **2017**, *4*, 1797–1808.
- [2] P. S. Francis, J. L. Adcock, N. W. Barnett, *Spectrochim. Acta Part A* **2006**, *65*, 708–710.
- [3] a) Z. Liu, W. Qi, G. Xu, *Chem. Soc. Rev.* **2015**, *44*, 3117–3142; b) E. H. Doeven, G. J. Barbante, C. F. Hogan, P. S. Francis, *ChemPlusChem* **2015**, *80*, 456–470; c) A. Kapturkiewicz, *Anal. Bioanal. Chem.* **2016**, *408*, 7013–7033; d) A. Fiorani, G. Valenti, E. Villani, M. Marcaccio, E. Rampazzo, L. Prodi, F. Paolucci, in *Luminescence in Electrochemistry* (Eds.: F. Misomandre, P. Audebert), Springer, Gewerbestrasse, Switzerland, **2017**, pp. 293–326; e) S. Laird, F. Hogan Conor, in *Iridium(III) in Optoelectronic and Photonics Applications* (Ed.: E. Zysman-Colman), John Wiley & Sons, Inc., Chichester, UK, **2017**, pp. 359–414.
- [4] E. H. Doeven, E. M. Zammit, G. J. Barbante, C. F. Hogan, N. W. Barnett, P. S. Francis, *Angew. Chem. Int. Ed.* **2012**, *51*, 4354–4357.
- [5] a) E. H. Doeven, E. M. Zammit, G. J. Barbante, P. S. Francis, N. W. Barnett, C. F. Hogan, *Chem. Sci.* **2013**, *4*, 977–982; b) E. H. Doeven, G. J. Barbante, E. Kerr, C. F. Hogan, J. A. Endler, P. S. Francis, *Anal. Chem.* **2014**, *86*, 2727–2732.
- [6] M. A. Haghighatbin, S.-C. Lo, P. L. Burn, C. F. Hogan, *Chem. Sci.* **2016**, *7*, 6974–6980.
- [7] a) W. Sun, S. Sun, N. Jiang, H. Wang, X. Peng, *Organometallics* **2015**, *34*, 3385–3389; b) W. Sun, S. Sun, N. Jiang, L. Gao, G. Zheng, *J. Organomet. Chem.* **2017**, *846*, 367–371.
- [8] a) H. Li, L. Bouffier, S. Arbault, A. Kuhn, C. F. Hogan, N. Sojic, *Electrochem. Commun.* **2017**, *77*, 10–13; b) Y.-Z. Wang, C.-H. Xu, W. Zhao, Q.-Y. Guan, H.-Y. Chen, J.-J. Xu, *Anal. Chem.* **2017**, *89*, 8050–8056.
- [9] S. E. Fosdick, K. N. Knust, K. Scida, R. M. Crooks, *Angew. Chem. Int. Ed.* **2013**, *52*, 10438–10456.
- [10] L. Bouffier, S. Arbault, A. Kuhn, N. Sojic, *Anal. Bioanal. Chem.* **2016**, *408*, 7003–7011.
- [11] a) H.-R. Zhang, Y.-Z. Wang, W. Zhao, J.-J. Xu, H.-Y. Chen, *Anal. Chem.* **2016**, *88*, 2884–2890; b) A. de Poulpiquet, B. Diez-Buitrago, M. Milutinovic, B. Goudeau, L. Bouffier, S. Arbault, A. Kuhn, N. Sojic, *ChemElectroChem* **2016**, *3*, 404–409; c) A. de Poulpiquet, B. Diez-Buitrago, M. D. Milutinovic, M. Sentic, S. P. Arbault, L. Bouffier, A. Kuhn, N. Sojic, *Anal. Chem.* **2016**, *88*, 6585–6592.
- [12] Y.-Z. Wang, W. Zhao, P.-P. Dai, H.-J. Lu, J.-J. Xu, J. Pan, H.-Y. Chen, *Biosens. Bioelectron.* **2016**, *86*, 683–689.
- [13] A. J. Bard (Ed.), *Electrogenerated Chemiluminescence*, Marcel Dekker, New York, **2004**, p. 540.
- [14] E. Kerr, E. H. Doeven, G. J. Barbante, C. F. Hogan, D. Bower, P. S. Donnelly, T. U. Connell, P. S. Francis, *Chem. Sci.* **2015**, *6*, 472–479.
- [15] a) H. C. Moon, T. P. Lodge, C. D. Frisbie, *J. Am. Chem. Soc.* **2014**, *136*, 3705–3712; b) K. N. Swanick, M. Sandroni, Z. Ding, E. Zysman-Colman, *Chem. Eur. J.* **2015**, *21*, 7435–7440; c) E. Kerr, E. H. Doeven, G. J. Barbante, C. F. Hogan, D. J. Hayne, P. S. Donnelly, P. S. Francis, *Chem. Sci.* **2016**, *7*, 5271–5279.
- [16] a) D. Bruce, M. M. Richter, *Anal. Chem.* **2002**, *74*, 1340–1342; b) G. J. Barbante, N. Kebede, C. M. Hindson, E. H. Doeven, E. M. Zammit, G. R. Hanson, C. F. Hogan, P. S. Francis, *Chem. Eur. J.* **2014**, *20*, 14026–14031.
- [17] D. Laser, A. J. Bard, *J. Electrochem. Soc.* **1975**, *122*, 632–40.
- [18] E. H. Doeven, G. J. Barbante, A. J. Harsant, P. S. Donnelly, T. U. Connell, C. F. Hogan, P. S. Francis, *Sens. Actuators B* **2015**, *216*, 608–613.

Manuscript received: March 6, 2018

Version of record online: May 8, 2018