## Mixed annihilation electrogenerated chemiluminescence of iridium(III) complexes

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Mixed annihilation electrogenerated chemiluminescence of iridium(III) complexes

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Previously reported annihilation ECL of mixtures of metal complexes have generally comprised Ir(ppy)₃ or a close analogue as a higher energy donor/emitter (green/blue light) and [Ru(bpy)₃]²⁺ or its derivative as a lower energy acceptor/emitter (red light). In contrast, here we examine Ir(ppy)₃ as the lower energy acceptor/emitter, by combining it with a second Ir(III) complex: [Ir(df-ppy)₂(ptb)]⁺ (where ptb = 1-benzyl-1,2,3-triazol-4-ylpyridine). The application of potentials sufficient to attain the first single-electron oxidation and reduction products can be exploited to detect Ir(ppy)₃ at orders of magnitude lower concentration, or enhance its maximum emission intensity at high concentration far beyond that achievable through conventional annihilation ECL of Ir(ppy)₃ involving comproportionation. Moreover, under certain conditions, the colour of the emission can be selected through the applied electrochemical potentials. We have also prepared a novel Ir(III) complex with a sufficiently low reduction potential that the reaction between its reduced form and Ir(ppy)₃⁺ cannot populate the excited state of either luminophore. This enabled, for the first time, the exclusive formation of either excited state through the application of higher cathodic or anodic potentials, but in both cases, the ECL was greatly diminished by parasitic dark reactions.

Introduction

Iridium(III) complexes have emerged as promising alternatives to the traditional ruthenium(II) complexes utilised in electrogenerated chemiluminescence (ECL) systems.¹ ² The introduction of these novel electrochemiluminophores was predominantly focussed on improving ECL efficiencies,³ ⁴ but Bruce and Richter were also quick to show that the wider range of emission colours from Ir(III) complexes could be exploited for simultaneous multi-colour co-reactant ECL from mixtures of Ir(III) and Ru(II) complexes.⁵ Despite the promising early demonstration by Richter’s group and the plethora of new Ir(III) and other metal complexes that were synthesised and tested in subsequent ECL studies, surprisingly few multi-colour metal-complex ECL systems were reported over the following decade.⁶

In 2012, however, several co-reactant ECL systems were reported in which the distinct redox character of the electrochemiluminophores was exploited to control the formation of different emitting species,⁷ stimulating new interest in the development of multi-colour ECL systems.² ⁸ Subsequent reports have included electrochemically tuneable multi-coloured co-reactant ECL from multiple metal complexes,⁹ heterodinuclear Ru(II)/Ir(III) complexes,¹⁰ a single Ir(III) complex,¹¹ and combinations of different ECL systems.¹² Moreover, the annihilation ECL of mixtures of Ru(II) and Ir(III) complexes was explored for the first time.¹³⁻¹⁷ Unlike co-reactant ECL, where only an oxidative or a reductive potential is applied, the annihilation mode of ECL involves the alternating application of oxidative and reductive potentials, with subsequent reactions between the oxidised and reduced metal complexes generating the excited state responsible for the emission.¹¹ ¹² ¹⁷ In mixed annihilation ECL systems, the multiple oxidation and reduction potentials of the metal complexes offer a simple means to control the generation of more than one excited state, and therefore the overall colour of the emission. With this in mind, Moon et al.¹³ sought to fabricate a colour-tuneable ECL-based light-emitting device comprising two luminophores ([Ru(bpy)₃]Cl₂ and [Ir(df-ppy)₂(bpy)][PF₆]₃; see Fig. 1a). Under the applied conditions, the orange-red ECL of the Ru(II) complex was enhanced two-fold, but the characteristic green ECL from the Ir(III) complex was...
not observed. Similarly, Swanick et al.15 examined the annihilation and co-reactant ECL of a [Ru(dtb-bpy)3]3+/2+ ‘soft salt’ (and the related combination of [Ru(dtb-bpy)3]3+/2+ and TBA[Ir(ppy)3]2+/1+) (Fig. 1b) dissolved in acetonitrile and observed only the orange-red emission of the Ru(II) complex.

Figure 1. Combinations of metal complexes used in three previous annihilation ECL studies.13-16 Electrochemical potentials are referenced to Fc0/+. Data from reference 14.

Figure 2. (a) Corrected photoluminescence emission spectra and (b) cyclic voltammograms for [Ru(bpy)3]3+/2+ (red line), Ir(ppy)3 (green line), [Ir(df-ppy)2(ptb)]2+ (blue line) and [Ir(df-ppy-CF3)2(ptb)]2+ (black line) in dry acetonitrile at room temperature. The spectra were obtained using a metal complex concentration of 10 μM, using excitation wavelengths of 450, 350, 310 and 260 nm, respectively, with appropriate excitation and emission filters (see also Fig. S1). The CVs were obtained at 200 μM with 0.1 M TBAPF6 supporting electrolyte, at a scan rate of 0.1 V s⁻¹, using a glassy carbon working electrode, platinum wire counter electrode and silver wire reference electrode. Prior to collecting the CVs, the solutions were degassed for 15 min. The dotted line (1) shows the minimum potential required to generate Ir(ppy)3* upon reaction with Ir(ppy)3. For example, the [Ru(bpy)3]3+/2+ couple is on the right side of the line, and so the reaction of [Ru(bpy)3]3+ and Ir(ppy)3* does not generate Ir(ppy)3*, whereas the [Ru(bpy)3]3+/2+ couple is on the left side of the line, and the reaction of [Ru(bpy)3]3+ and Ir(ppy)3* can generate Ir(ppy)3* (i.e. Equation 7).

Simple estimations of the exergonicity14, 16, 18 of reactions between the redox states available in this system (Fig. 2b) indicate that the least powerful reductant capable of generating Ir(ppy)3* upon reaction with Ir(ppy)3* was the 3e⁻ reduced state of [Ru(bpy)3]3+/2+ (Equations 5-8). When the cathodic pulse was moved sufficiently negative to generate [Ru(bpy)3]2+*, the green emission from Ir(ppy)3* (via Equation 7) and the orange-red emission from [Ru(bpy)3]3+/2+* (via Equation 3) both occurred, which was perceived visually as yellow light.

We previously investigated the annihilation ECL of [Ru(bpy)3]3+/2+ and various Ir(III) complexes (e.g., Fig. 1c), and under suitable conditions, we observed emission from one or both luminophores, depending on which electrochemical potentials were applied.14 In a mixture of [Ru(bpy)3]3+ and Ir(ppy)3, for example, the Ir(III) complex is easier to oxidise and the Ru(II) complex is more readily reduced (Fig. 2b). We can therefore alternately apply positive and negative potentials that will only oxidise the Ir(III) complex and only reduce the Ru(II) complex. Subsequent electron transfer between these two species provides sufficient energy to attain the excited state [Ru(bpy)3]3+/2+* (Equations 1-4), but not Ir(ppy)3*. Thus, only the characteristic orange-red luminescence of the Ru(II) complex (Fig. 2a) was observed.14

Equation 1: [Ru(bpy)3]3+ + e⁻ → [Ru(bpy)3]2+
Equation 2: Ir(ppy)3 – e⁻ → Ir(ppy)3*
Equation 3: [Ir(ppy)3]3+ + [Ru(bpy)3]2+ → Ir(ppy)3 + [Ru(bpy)3]3+/2+*
Equation 4: [Ru(bpy)3]3+ → [Ru(bpy)3]2+ + hv

Equation 5: [Ru(bpy)3]2+ + e⁻ → [Ru(bpy)3]1+
Equation 6: [Ru(bpy)3]1+ → [Ru(bpy)3]0
Equation 7: Ir(ppy)3* → Ir(ppy)3+ (via Equation 5)
Equation 8: [Ru(bpy)3]3+/2+* → [Ru(bpy)3]3+/2+ (via Equation 3)
(7) \[\text{Ir}(ppy)_3^{3+} + [\text{Ru(bpy)}_3]^{2+} \rightarrow \text{Ir}(ppy)_3^{2+} + [\text{Ru(bpy)}_3]^{0}\]

When the cathodic pulse was moved further negative to reduce \(\text{Ir}(ppy)_3\) (Fig. 2b), the emission from the green luminophore was markedly increased through its comproportionation (Equation 9), and the formation of \([\text{Ru(bpy)}_3]^{2+}\) was inhibited by an irreversible fourth reduction of the ruthenium complex, resulting in a predominantly green emission.\(^{16}\)

\[\text{Ir}(ppy)_3^{3+} + [\text{Ir(df-ppy-CF}_3)_2]^{2+} \rightarrow \text{Ir}(ppy)_3^{2+} + [\text{Ir(df-ppy-CF}_3)_2]^{+}\] (9)

The investigations of multi-colour annihilation ECL with mixtures of metal complexes to date\(^{13-16}\) have each focussed on a combination of \([\text{Ru(bpy)}_3]^{2+}\) (or its di-t-butyl-bipyridine derivative) and an Ir(III) complex that emits green or blue light. In each case, electron and/or energy transfer between iridium and ruthenium species favoured the formation of the excited state of the Ru(II) complex,\(^{16}\) often resulting in emission exclusively from that luminophore.\(^{13, 15}\) Moreover, in each case, the reaction between the most readily formed oxidation and reduction products provided sufficient energy to generate the excited state ruthenium complex (e.g., Equation 3). It was therefore not possible to apply potentials that would generate the excited state Ir(III) complex in the absence of any energetically feasible pathways to form the excited state Ru(II) complex.

Herein we first demonstrate the annihilation ECL of a mixture of two Ir(III) complexes: \(\text{Ir}(ppy)_3\) (Fig. 1c, right) and \(\text{Ir(df-ppy-CF}_3)_2\) (Fig. 3a), which emit green and blue light, respectively. Unlike previous reports, in which the \(\text{Ir}(ppy)_3\) complex was the higher energy emitter that was partially quenched in the presence of the Ru(II) complex, in this study, \(\text{Ir}(ppy)_3^{*}\) is the longer wavelength emitter, which we anticipated to be favoured over the formation of the higher energy \([\text{Ir(df-ppy-CF}_3)_2]^{*}\). Secondly, we prepared a novel blue luminophore \([\text{Ir(df-ppy-CF}_3)_2]^{*}\) (Fig. 3b) with a reduction potential of sufficiently low magnitude that the reaction between its reduced form and the oxidised \(\text{Ir}(ppy)_3^{*}\) cannot attain the excited state of either luminophore (i.e. neither \([\text{Ir(df-ppy-CF}_3)_2]^{*}\) nor \(\text{Ir}(ppy)_3^{*}\)). This enables the selective formation of either excited state through the application of higher cathodic or anodic potentials.

**Results and discussion**

**Annihilation ECL from a mixture of two Ir(III) complexes**

For these experiments, we selected \(\text{Ir}(ppy)_3\) and \(\text{Ir(df-ppy-CF}_3)_2\), as two complexes possessing sufficiently dissimilar emission wavelengths (Fig. 2a and S1; Table 1) and redox potentials (Fig. 2b; Table 2).

**Table 1. Spectroscopic properties**

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<th>Complex</th>
<th>Absorbance</th>
<th>Photoluminescence*</th>
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<tr>
<td></td>
<td>(\lambda_{\text{ex/em}}) nm</td>
<td>t.r. (\lambda_{\text{ex}})/nm (eV) (K, \lambda_{\text{em}})/nm (eV)</td>
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<tr>
<td>(\text{Ir}(ppy)_3^{3+})</td>
<td>243, 286, 420/450</td>
<td>622 (1.99) 581 (2.13), 629</td>
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<tr>
<td>(\text{Ir}(ppy)_3^{2+})</td>
<td>240, 281, 373</td>
<td>520 (2.38) 494 (2.51), 531, 578</td>
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<tr>
<td>(\text{Ir(df-ppy-CF}_3)_2^{3+})</td>
<td>245, 302/359</td>
<td>453 (2.74), 488 (2.77), 480, 483</td>
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<tr>
<td>(\text{Ir(df-ppy-CF}_3)_2^{2+})</td>
<td>249, 266, 302/495</td>
<td>470 (2.64), 495, 495, 525</td>
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*Corrected for the change in instrument sensitivity across the wavelength range (Fig. S1). The correction factor was established by using a light source with standard spectral irradiance.\(^{16}\) Values obtained at 77 K include 580 nm by our group,\(^{19}\) and Kawanishi et al.,\(^{20}\) and 582 nm by Juris et al.\(^{21}\) Our group\(^{19}\) and Dedeian et al.\(^{11}\) reported a \(\lambda_{\text{ex}}\) of 494 nm for \(\text{Ir}(ppy)_3\) in EtOH-MeOH glasses at 77 K.

**Table 2. MO energies and electrochemical potentials**

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<tr>
<th>Complex</th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
<th>M/M*</th>
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<tr>
<td>(\text{Ir}(ppy)_3^{3+})</td>
<td>-5.046</td>
<td>-3.278</td>
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<tr>
<td>(\text{Ir}(ppy)_3^{2+})</td>
<td>-6.262</td>
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<tr>
<td>(\text{Ir(df-ppy-CF}_3)_2^{3+})</td>
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<tr>
<td>(\text{Ir(df-ppy-CF}_3)_2^{2+})</td>
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<td>-2.013</td>
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<td>-1.88</td>
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<tr>
<td>(\text{Ir(df-ppy-CF}_3)_2^{2-})</td>
<td>-5.432</td>
<td>-2.013</td>
<td>1.35</td>
<td>-1.88</td>
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Cyclic voltammetry; electrodes: glassy carbon working, silver wire reference, platinum wire counter; 0.2 mM metal complex in dry ACN with 0.1 M TBAPF\(_6\); solution degassed for 15 min prior to analysis; scan rate: 0.1 V s\(^{-1}\).* Predicted from the difference in LUMO energies from those of the \([\text{Ir(df-ppy-CF}_3)_2]^{3+}\) complex. The MO energies for all metal complexes discussed in this study are shown in Fig. S12.
Due to the strong σ-donation of its Ir-C bonds, the Ir(ppy)$_3$ complex (exhibiting a mixed metal-ligand HOMO and a ligand-based LUMO) is readily oxidised but difficult to reduce. The introduction of the electron-withdrawing fluoro substituents on the phenyl rings stabilises the HOMO and to a lesser extent, the LUMO energy level. This results in a positive shift in the reduction potential and to a lesser extent, the oxidation potential, and a hypsochromic shift in the emission, without significant change to the quantum yield (0.99). The replacement of one df-ppy ligand in Ir(df-ppy)$_3$ with the substituted triazolopyridine ligand (ptb) results in even greater MO stabilisation, more positive redox potentials, and a further blue-shift in luminescence. Despite its lower photoluminescence quantum yield (0.21), [Ir(df-ppy)$_3$] produces more intense co-reactant ECL with TPrA and several close analogues have been reported to exhibit greater annihilation ECL efficiencies than Ir(ppy)$_3$.

Although [Ir(df-ppy)$_2$(ptb)]$^0$ is reduced at a much less negative potential than that of Ir(ppy)$_3$ (Fig. 2b), the reaction of [Ir(df-ppy)$_2$(ptb)]$^0$ and [Ir(ppy)$_3$]$^*$ should still generate Ir(ppy)$_3^*$ (Equation 10), based on: (i) an estimation of reaction exergonicity comparing the redox potentials with the excited MLCT state energy; (ii) the similarity of the [Ir(df-ppy)$_2$(ptb)]$^0$ couple (-2.12 V vs Fc$^{+/0}$) with [Ru(bpy)$_3$]$^0$ (-2.15 V vs Fc$^{+/0}$), which we previously observed as the least negative redox couple of the ruthenium complex that was capable of eliciting the Ir(ppy)$_3^*$ excited state upon reaction with [Ir(ppy)$_3$]$^*$ (Equation 7); and (iii) the cut-off reduction potential (approximately -2.10 V vs Fc$^{+/0}$) for efficient mixed ECL from organic nitriles/ketones with Ir(ppy)$_3$ reported by Kapturkiewicz and Angulo. The feasibility of this reaction is supported by comparison of the calculated [Ir(df-ppy)$_2$(ptb)]$^0$ SOMO and [Ir(ppy)$_3$]$^*$ LUMO energies (Fig. 4a).

\[
\text{[Ir(ppy)$_3$]}^* + \text{[Ir(df-ppy)$_2$(ptb)]}^0 \rightarrow \text{Ir(ppy)$_3$}^* + \text{[Ir(df-ppy)$_2$(ptb)]}^* \tag{10}
\]

We examined the annihilation ECL from mixtures of [Ir(df-ppy)$_2$(ptb)]$^0$ and Ir(ppy)$_3$ at various concentrations (in acetonitrile with 0.1 TBAPF$_6$) using alternating electrochemical potentials: one sufficient to oxidise only Ir(ppy)$_3$ or both complexes, and the other sufficient to reduce only [Ir(df-ppy)$_2$(ptb)]$^0$ or both complexes, thus giving four sets of applied potentials (Expt (i)-(iv) shown in Fig 5a).

![Figure 4. MO energies of [Ir(df-ppy)$_2$(ptb)]$^0$, [Ir(df-ppy-CF$_3$(ptb)]$^0$ and [Ir(ppy)$_3$]$^*$, relevant to generation of Ir(ppy)$_3^*$. The MO energies for all metal complexes discussed in this study are shown in Fig. S12.](image)

![Figure 5. (a) An illustration of the four different sets of potentials applied to the mixture of Ir(ppy)$_3$ and [Ir(df-ppy)$_2$(ptb)]$^0$ (Expts (i)-(iv)), with cyclic voltammograms of the two Ir(III) complexes shown beneath. (b,c) ECL spectra for a mixture of 0.2 mM [Ir(df-ppy)$_2$(ptb)]$^0$ and varying concentrations (0.1, 1 and 10 µM) of Ir(ppy)$_3$ using (b) Expt (i) or (c) Expt (iii). (d) ECL spectra for a mixture of 0.2 mM [Ir(df-ppy)$_2$(ptb)]$^0$ and 1 µM Ir(ppy)$_3$, using each of the four sets of applied potentials (Expt (i)-(iv)). In each case, the two-step potential was applied at 10 Hz for 12 s. The lower structural detail in the emission from [Ir(df-ppy)$_2$(ptb)]$^0$ here compared to the photoluminescence emission shown in Fig. 2a is due to the lower spectral resolution of the instrumentation used to collect ECL spectra. In Fig. 5b, the ECL intensity at 10 µM Ir(ppy)$_3$ was 28-fold greater than at 1 µM.](image)
In Expt (i), in which only Ir(ppy)$_3$ was oxidised and only [Ir(df-ppy)$_2$(ptb)$]^+$ was reduced, the spectral distribution matched that of the Ir(ppy)$_3$ emission, without any contribution from [Ir(df-ppy)$_2$(ptb)$]^+$ (Fig. 5b). The ECL from this system increased in intensity with greater concentrations of Ir(ppy)$_3$ and/or [Ir(df-ppy)$_2$(ptb)$]^+$ (up to at least the highest concentration examined, 0.2 mM). This had two useful consequences: firstly, in the presence of 0.2 mM [Ir(df-ppy)$_2$(ptb)$]^+$, the Ir(ppy)$_3$ complex could be detected down to nanomolar levels – many orders of magnitude below what could be observed by the annihilation ECL of Ir(ppy)$_3$ (in the absence of [Ir(df-ppy)$_2$(ptb)$]^+$) with this instrumental configuration. Secondly, the intensity of the mixed annihilation ECL between high concentrations of Ir(ppy)$_3$ and [Ir(df-ppy)$_2$(ptb)$]^+$ far exceeded the maximum intensity of the annihilation ECL of Ir(ppy)$_3$, which is limited by its solubility in acetonitrile. The ECL of a mixture of 0.2 mM Ir(ppy)$_3$ and 0.2 mM [Ir(df-ppy)$_2$(ptb)$]^+$ exhibited an intensity that was ~19-fold greater than the annihilation ECL of 0.2 mM Ir(ppy)$_3$ alone. We attribute this to part species available at the electrode surface during the alternating electrochemical potentials. When the reductive potential is applied in the mixed system, there is a supply of [Ir(df-ppy)$_2$(ptb)$]^+$ that was not oxidised in the previous pulse.

Similarly, when the oxidative potential is applied, there is a pool of Ir(ppy)$_3$ that was inert to the previous reductive pulse. Moreover, the mixed system exhibited greater annihilation ECL efficiency (by 2.9-fold at a concentration of 0.1 mM). This is consistent with Kapturkiewicz and Angulo’s observation that the mixed annihilation ECL of Ir(ppy)$_3$ is 2.5-fold with the radical anions of aromatic nitrites and ketones (where the $\Delta G_{as}$ was between ~0 and -0.36 eV) exhibited greater ECL efficiencies than the annihilation ECL of Ir(ppy)$_3$ alone ($\Delta G_{as}$ -0.51 eV), where the reduced efficiency was tentatively attributed to additional parasitic processes occurring at the large negative potentials required for the reduction of Ir(ppy)$_3$.

If we repeat the above experiment, but move the reductive pulse further negative, so that both [Ir(df-ppy)$_2$(ptb)$]^+$ and Ir(ppy)$_3$ are reduced (Fig. 5a, Expt (ii)), there are now two pathways to the Ir(ppy)$_3$* emitter (Equations 10 and 9). The application of this wider potential range, however, diminishes the ECL intensity (for example, compare plots (i) and (ii) in Fig. 5d). This appears to arise from at least two factors: firstly, at potentials sufficiently negative to reduce Ir(ppy)$_3$, the [Ir(df-ppy)$_2$(ptb)$]^0$ species is subject to further irreversible reductions (Fig 53a, blue plot). Secondly, the applied reductive potential nears the edge of the potential window, inviting deleterious reactions with the solvent, particularly if traces of water are present. This may play a role in the greater efficiency of the mixed ECL system (Equation 10) compared to the annihilation ECL of Ir(ppy)$_3$, in the absence of [Ir(df-ppy)$_2$(ptb)$]^+$ as described above.

In Expt (iii), in which appropriate potentials were applied to oxidise both Ir(ppy)$_3$ and [Ir(df-ppy)$_2$(ptb)$]^+$, but reduce only [Ir(df-ppy)$_2$(ptb)$]^+$, the spectral distribution of the resulting ECL can comprise contributions from both Ir(ppy)$_3$* (Equation 10) and [Ir(df-ppy)$_2$(ptb)$]^+$ (Equation 11). The ratio of these contributions was highly dependent on the concentrations of the two complexes (Fig. 5c and S6). There is considerable overlap between the luminescence of Ir(ppy)$_3$ and [Ir(df-ppy)$_2$(ptb)$]^+$, but their relative contributions to the ECL can be readily quantified by deconvolution of the overall emission into their characteristic spectra (Fig. 54). In a few cases, there was some deviation from the model, particularly on the longer wavelength side of the emission, which we attribute to the overlap of the shorter wavelengths of the [Ir(df-ppy)$_2$(ptb)$]^+$ emission with the lowest energy absorption bands of Ir(ppy)$_3$ (Fig. S5a) and/or an unexpected subsequent oxidation of Ir(ppy)$_3$ at the high applied potential required to oxidise the [Ir(df-ppy)$_2$(ptb)$]^+$ complex (Fig. S3a, green plot).

$$\text{[Ir(df-ppy)$_2$(ptb)$]^2+ + [Ir(df-ppy)$_2$(ptb)$]^0 \rightarrow [Ir(df-ppy)$_2$(ptb)$]^+ + [Ir(df-ppy)$_2$(ptb)$]^+} \ (11)$$

When these potentials are applied to this mixed ECL system, it can be thought of as the annihilation ECL of [Ir(df-ppy)$_2$(ptb)$]^+$, quenched by the presence of Ir(ppy)$_3$ (Fig. 5c and S6). Using a mixture of 200 $\mu$M [Ir(df-ppy)$_2$(ptb)$]^+$ and 0.1 $\mu$M Ir(ppy)$_3$, the contribution of Ir(ppy)$_3$* to the emission was less than 0.01%. However, with [Ir(df-ppy)$_3$] at 1 $\mu$M and 10 $\mu$M, the contribution of Ir(ppy)$_3$* to the emission increased to 5.3% and 70.6%, and the overall emission intensity (integrated area) decreased by 2.1-fold and 4.8-fold, respectively. The efficient quenching of the ECL from [Ir(df-ppy)$_2$(ptb)$]^+$ in this mixed system most likely results from several processes, including electron transfers between ground and/or excited states (Equations 10, 12 and 13 and processes involving the further oxidation of Ir(ppy)$_3$, Fig. 53a, green plot) and direct energy transfer (Equation 14; Fig. 55a).

$$\text{[Ir(df-ppy)$_2$(ptb)$]^2+ + [Ir(df-ppy)$_2$(ptb)$]^0 \rightarrow [Ir(df-ppy)$_2$(ptb)$]^+ + [Ir(df-ppy)$_2$(ptb)$]^+} \ (12)$$

$$\text{[Ir(df-ppy)$_2$(ptb)$]^2+ + [Ir(df-ppy)$_2$(ptb)$]^0 \rightarrow [Ir(df-ppy)$_2$(ptb)$]^+ + [Ir(df-ppy)$_2$(ptb)$]^+} \ (13)$$

$$\text{[Ir(df-ppy)$_2$(ptb)$]^2+ + [Ir(df-ppy)$_2$(ptb)$]^0 \rightarrow [Ir(df-ppy)$_2$(ptb)$]^+ + [Ir(df-ppy)$_2$(ptb)$]^+} \ (14)$$

To complete this series of experiments, we applied alternating potentials sufficient to both oxidise and reduce both complexes (Fig. 5a, Expt (iv)). Similar to that described above, extending the potential range to include the reduction of Ir(ppy)$_3$ resulted in a decrease in ECL intensity (for example, compare plots (iii) and (iv) in Fig. 5d). In this case, where both luminophores can contribute to the emission, the reduction of Ir(ppy)$_3$ also increased its relative contribution to the emission.

Manipulating the redox potentials to switch off the cross-complex excitation

In all annihilation ECL involving mixtures of metal complexes reported to date, the application of the lowest anodic and cathodic potentials required for only the most facile oxidation and reduction still produced species capable of generating the lower energy excited state of the luminophores. In the novel system described above, this comprised the oxidation of Ir(ppy)$_3$ and reduction of [Ir(df-ppy)$_2$(ptb)$]^+$ (Expt (i) in Fig. 5a) to form species that react with sufficient energy to generate
the characteristic green ECL from Ir(ppy)$_3^+$ (Equation 10). In that case, however, the reduction potential of [Ir(df-ppy)$_3$(ptb)]$^+$ is only sufficient by 20-180 mV$^6$. We therefore sought to eliminate that pathway to generate the Ir(ppy)$_3^+$ emitter through a subtle modification of the [Ir(df-ppy)$_3$(ptb)]$^+$ structure that would stabilise the LUMO energy level.

The frontier MO character of [Ir(C$^N$N)$_2$(N$^N$)$_2$]$^+$ complexes in which C$^N$ is ppy or df-ppy, and N$^N$ is a 1-substituted 1,2,3-triazol-4-ylpyridine (Fig. 6a)$^{26, 28, 30}$ is generally akin to analogous complexes in which N$^N$ is a more commonly employed bipyridine-type ligand (Fig. 6b).$^{31-33}$ In these complexes, the HOMO is an admixture of the metal-centred d$\pi$ orbitals and phenyl $\pi$ orbitals of the C$^N$ ligands and the LUMO is normally associated with the neutral N$^N$ ancillary ligand. A change in reduction potential, as is desired in our study, is therefore often achieved through manipulation of the ancillary ligand. Implementing a less negative reduction potential in that manner would also induce a considerable bathochromic shift in the luminescence, and lessen the desired distinction with Ir(ppy)$_3^+$.

Despite the spatial separation of the frontier MOs of these complexes, manipulation of oxidation and reduction potentials is not entirely orthogonal. And whilst addition of further electron withdrawing groups to the df-ppy ligands could be anticipated to have a greater effect on the oxidation potential, it could also provide a sufficient change to the reduction potential for our purposes, without a large, deleterious bathochromic shift to the emission. With this approach, the novel analogue could potentially be prepared from one of several commercially available dimeric ([Ir(C$^N$N)$_2$(μ-Cl)$_2$])$_2$ precursors, where C$^N$ is one of the three df-ppy derivatives shown in Fig. 7.

None of the three proposed complexes had previously been prepared, but the calculated LUMO energies of the complexes predicted a change in reduction potential (relative to [Ir(df-ppy)$_3$(ptb)]$^+$ of +18 mV for [Ir(df(CF$_3$)-ppy-Me)$_3$(ptb)]$^+$, +111 mV for [Ir(df(CN)-ppy)$_3$(ptb)]$^+$ and +195 mV for [Ir(df-ppy-CF$_3$)$_3$(ptb)]$^+$ (Table 2). Moreover, calculation of SOMO energies for the reduced complexes, [Ir(df-ppy)$_3$(ptb)]$^+$ (-2.539 eV), [Ir(df(CF$_3$)-ppy-Me)$_3$(ptb)]$^+$ (-2.583 eV), [Ir(df(CN)-ppy)$_3$(ptb)]$^+$ (-2.723 eV) and [Ir(df-ppy-CF$_3$)$_3$(ptb)]$^+$ (-2.804 eV) showed that only the SOMO of [Ir(df-ppy-CF$_3$)$_3$(ptb)]$^+$ was lower in energy than the LUMO of [Ir(ppy)$_3^+$] (-2.787 eV) (Fig. 4b and S12).

For the two complexes with the additional electron withdrawing substituent on the phenyl ring of df-ppy (associated with the HOMO), relatively large shifts in oxidation potential were anticipated, resulting in hypsochromic shifts in the emission. The pyridyl ring is less commonly modified than the phenyl ring of the C$^N$ ligand or the ancillary N$^N$ ligand for electrochemical or spectroscopic modulation of [Ir(C$^N$N)$_2$(N$^N$)$_2$]$^+$ complexes,$^{34}$ but the approach has found application, such as in the [Ir(df-ppy-CF$_3$)$_3$(dbt-bpy)]$^+$ complex (where dtb-bpy = 4,4′-di-t-butyl-2,2′-bipyridine), which is widely employed as a photoredox catalyst.$^{35, 36}$ The addition of CF$_3$ to the pyridyl moiety of the df-ppy ligands within [Ir(df-ppy)$_3$(bpy)]$^+$ and [Ir(df-ppy)$_3$(dbt-bpy)]$^+$ imparts a considerable hypsochromic shift in their luminescence$^{36}$ but our calculations predict a small bathochromic shift upon addition of the CF$_3$ group to the same positions in the [Ir(df-ppy)$_3$(ptb)]$^+$ analogue.

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![Figure 6. (a,b) Simplified depiction of the spatial distribution of HOMO and LUMO typically calculated for [Ir(C$^N$N)$_2$(N$^N$)$_2$]$^+$ complexes, where C$^N$ is ppy, df-ppy or related ligands, and N$^N$ is (a) a triazolylpyridine or (b) a bipyridine type ligand. (c-d) BP86/def2-TZVP ground-state frontier molecular orbital contour plots for (c) [Ir(df-ppy)$_3$(ptb)]$^+$ and (d) [Ir(df-ppy-CF$_3$)$_3$(ptb)]$^+$. Additional contour plots are shown in Fig. S10.](image-url)

Figure 7. The C$^N$ ligands within the three commercially available [Ir(C$^N$N)$_2$(μ-Cl)$_2$])$_2$ precursors that we considered for the preparation of an [Ir(df-ppy)$_3$(ptb)]$^+$ analogue with a less negative reduction potential.

We therefore chose to prepare the [Ir(df-ppy-CF$_3$)$_3$(ptb)]$^+$ complex (as the hexafluorophosphate salt), for which the predicted difference in the reduction potential from the parent [Ir(df-ppy)$_3$(ptb)]$^+$ was greater than that required (20-180 mV) to leave the reaction between the reduced complex and
Ir(pppy)$_3^+$ with insufficient energy to generate Ir(pppy)$_3^*$. The novel [Ir(df-ppy-CF$_2$)$_2$(ptb)][PF$_6$] was synthesised based on our previously reported procedure$^{26,37}$ and characterised by multinuclear ($^{1}$H, $^{13}$C, $^{19}$F) homo- and heteronuclear NMR spectroscopy. High resolution mass spectrometry revealed a single molecular species corresponding to the cation [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$, with its characteristic isotopic pattern, in excellent agreement with the calculated m/z value. Crystals of [Ir(df-ppy-CF$_2$)$_2$(ptb)][PF$_6$] suitable for single crystal X-ray crystallography were obtained and the solved structure revealed a distorted octahedral C$_2$N$_4$ environment around the central Ir(III) cation (Fig. 3c). The cyclometalating ligands were in a N,N-trans arrangement consistent with the geometry of the Ir(III) precursor. The ptb ligand occupied the final two coordination sites in a bidentate fashion, bound through the CF$_2$ group exerts a strong stabilising effect on higher unoccupied MOs associated with the p* orbitals of the pyridine rings of the df-ppy ligands, but they remain above the N,N-ligand based LUMO$^{31,38,39}$. In this case, the greater influence on the oxidation than the reduction potential is a consequence of the greater stabilising effect of the CF$_2$ substituent on the p* orbitals of the phenyl ring on the same ligand (contributing to the HOMO), than on those of the ancillary N,N ligand (contributing to the LUMO). The lowest energy triplet of [Ir(df-ppy)$_2$(dtb-bpy)]$^+$ exhibits $\Delta MLCT/LLCT$ (HOMO→LUMO) character$^{36}$ and the increase in the HOMO-LUMO gap is accompanied by a hyperschomophic shift in the emission.

The [Ir(df-ppy)$_2$(ptb)]$^+$ complex also exhibits a N,N-ligand based LUMO (Fig. 6a and 6c), but it is considerably higher in energy than that of [Ir(df-ppy)$_2$(dtb-bpy)], as seen in the difference in their reduction potentials of over 300 mV (Table S1). In this case, the stabilising effect of the CF$_2$ groups creates a new LUMO from one of the higher unoccupied MOs associated with the pyridine p* orbitals (Fig. 6d and S11). Based on the observed oxidation potentials (Table S1), the stabilisation of the HOMO is similar to that in the [Ir(df-ppy-CF$_2$)$_2$(dtb-bpy)]$^+$ complexes, but in the ptb analogue it is marginally outweighed by the decrease in LUMO energy, with a corresponding small bathochromic shift in the mixed 3MLCT/3LC emission. The emission spectra of [Ir(df-ppy)$_2$(ptb)]$^+$ and [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ show resolved vibronic structure (consistent with other [Ir(C$^N$N)$_2$(L)]$^+$ complexes in which L is a 1,2,3-triazole ligand) due to some mixing between the 3MLCT and 3LC states$^{29,30,37,41}$.

Upon application of alternating anodic and cathodic potentials at the working electrode that were sufficient to oxidise Ir(pppy)$_3$ and reduce [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ (Fig. 8a, Expt v), no significant ECL emission was observed (Fig. S9). By design, the subsequent reaction of the oxidised and reduced complexes is not sufficiently exergonic to generate the excited state Ir(pppy)$_3^*$ species (unlike Equation 10). Nevertheless, the ‘dark’ reaction to ground state products (Equation 15) can still occur.

$$\text{[Ir(pppy)$_3$]}^+ + \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^0 \rightarrow \text{[Ir(pppy)$_3$]} + \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^*$$  \tag{15}

When we adjusted the oxidative pulse to a potential sufficient to oxidise both complexes (Fig. 8a, Expt vii) the annihilation ECL of [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^0$ can occur (Equation 16).

$$\text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^2+ + \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^0 \rightarrow \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^* + \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^+$$  \tag{16}

The annihilation ECL of [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ was quenched by Ir(pppy)$_3$ (Fig. 8b) even more efficiently than that of [Ir(df-ppy)$_2$(ptb)]$^+$ (Fig. 5c and S8). Bearing in mind the similarities in their spectroscopic and electrochemical properties, we assume the same processes for quenching espoused for the annihilation of [Ir(df-ppy)$_2$(ptb)]$^+$ operate in this case, except that the reaction between the mixed oxidised and reduced species can only lead to the ground state product (Equation 15). Considering the absence of a significant contribution from Ir(pppy)$_3$ to the ECL of this system (Fig. 8b), we conclude that the observed contribution from Ir(pppy)$_3$ in the analogous ECL from the [Ir(df-ppy)$_2$(ptb)]$^+$ system (Fig. 5c) predominantly arose from electron transfer (Equation 10) rather than energy transfer (Equation 14) (although we acknowledge that the overlap between the emission of [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ with the absorption bands of Ir(pppy)$_3$ (Fig. S7a) is slightly lower than that of [Ir(df-ppy)$_2$(ptb)]$^+$ (Fig. S5a)). If we instead apply alternating potentials suitable for the annihilation ECL of Ir(pppy)$_3$ (Expt vii), both complexes will be reduced, but only Ir(pppy)$_3$ will be oxidised. Similar to the quenching of the annihilation ECL of [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ in the presence of the Ir(pppy)$_3$, described above, the annihilation ECL of Ir(pppy)$_3$ was effectively quenched by the presence of [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ (Fig. 8c), which in this case can be attributed to a combination of the mixed dark reactions (Equations 15 and 17), including those involving the further reduction of [Ir(df-ppy-CF$_2$)$_2$(ptb)]$^+$ (Fig. S3b) (e.g., Equation 18) and oxidative quenching of Ir(pppy)$_3^+$ (Equation 19).

$$\text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^2+ + \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^0 \rightarrow \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^* + \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^+$$  \tag{17}

$$\text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^0 + \text{[Ir(pppy)$_3$]} \rightarrow \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]} + \text{[Ir(pppy)$_3$]}$$  \tag{18}

$$\text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^+ + \text{[Ir(pppy)$_3$]}^+ \rightarrow \text{[Ir(df-ppy-CF$_2$)$_2$(ptb)]}^0 + \text{[Ir(pppy)$_3$]}^*$$  \tag{19}
advantages over conventional annihilation ECL involving comproportionation reactions. The combination of two electroactive species enables one to be detected at exceeding low concentrations when the other is in excess. Moreover, it could improve the operational parameters of simple ECL-based light-emitting devices across a range of visible emission colours, including lower operating power (for example, the mixed annihilation ECL of Ir(ppy)₃ and [Ir(df-ppy)(ptb)]⁺ has an ΔE of 2.45 eV compared to 3.00 eV for the annihilation ECL of Ir(ppy)₃ alone), greater ECL efficiencies (by avoiding parasitic reactions at extreme potentials) and greater overall emission intensities than either individual annihilation ECL system. Within these devices, however, the solubility of the luminophores within the matrix must also be optimised.

One remaining outcome of an ECL reaction between the electrochemically oxidised Ir(ppy)₃ and the first reduction product of another electrochemiluminophore, which was not included here, is where there is sufficient energy to attain the excited state of either electrochemiluminophore. This would require two luminophores with a similar difference between their first oxidation and first reduction potentials (ΔE) and therefore comparable emission colour. In that case, the dominant emitter from the electrochemiluminophores may also be influenced by differences in their luminescence quantum yield and/or the kinetic advantage of ligand-to-ligand electron transfer (where the electrochemically oxidised electron-accepting luminophore is excited) over metal-to-metal electron transfer (where the electrochemically reduced electron-donating luminophore is excited).²³

If we apply potentials beyond the first oxidation and first reduction of either complex, then there are of course other combinations of species for which the free energy of their reaction exceeds that required to generate either excited state (for example, the reaction of Ir(ppy)₃⁺ and [Ir(df-ppy)(ptb)]⁺ formed in Expt (iiii), Fig. 5d). These species, however, cannot be generated in isolation from the more facile oxidation and/or reduction products (which are Ir(ppy)₃ and [Ir(df-ppy)(ptb)]⁺ in the above example), and their reactions are vulnerable to other interferences as described in the previous section. Generally, electron transfer at anodic and cathodic potentials beyond the first oxidation of the most easily oxidised luminophore and the first reduction of the most easily reduced luminophore initiates multiple competing annihilation ECL reactions. In both the [Ir(ppy)₃][Ir(df-ppy)(ptb)]⁺ and the [Ir(ppy)₃][Ru(bpy)₃]²⁺ systems, and the large difference in the energy of the electronically excited states of the two luminophores appears to be the dominant factor in the relative emission intensities. In both systems, an excess in the concentration of the higher energy luminophore can be used to balance the intensities, so that the dominant emitter can be determined through the selection of applied potentials to manipulate the species generated at the electrode surface (e.g., Fig. 5d).

The ability to eliminate the efficient annihilation ECL from the [Ir(ppy)₃][Ir(df-ppy)(ptb)]⁺ system through subtle change in ligand structure highlights the ease in which these light-producing reactions can be manipulated, considering simple
estimations of reaction exergonicity and DFT-modelling based predictions of reduction and oxidation potentials. The absence of ECL from the reaction of Ir(ppy)$_{3}$ and [Ir(df-ppy-CF$_3$)$_2$(ptb)]$^0$ removes its contribution to the ECL of either isomerisation reaction (Equations 9 and 16), but in this particular combination, the generation of either excited state is subject to parasitic processes that result in ECL that is much less intense than that observed in the absence of the other luminophore.

**Experimental**

**Chemicals**

Tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate ([Ru(bpy)$_3$]$_2$)(PF$_6$)$_4$; tetrabutylammonium hexafluorophosphate (TBAPF$_6$); electrochemical grade) and dichlorotetrakis[3,5-difluoro-2-(2-pyridyl)phenyl]iridium(III) ([Ir(df-ppy)$_2$(μ-Cl)$_2$]) were purchased from Sigma-Aldrich (NSW, Australia). The other Ir(III) dimer (di-μ-chlorotetrakis[3,5-difluoro-2-[3-trifluoromethyl-2-pyridinyl]-kN]phenyl-kC)diiridium(III); [Ir(df-ppy-CF$_3$)$_2$(μ-Cl)]$_2$) and bis(cyclopentadienyl)iron (ferrocene), were purchased from Strem Chemicals (MA, USA). Acetonitrile was from Scharlau (Barcelona, Spain) and was distilled over calcium hydride under a nitrogen atmosphere in darkness under an inert atmosphere for approximately 15 minutes prior to analysis.

Potassium chloride for reference electrode was then removed and the residue dissolved in acetonitrile (2H, d, J = 8.9 Hz, phenyl-H), 5.71 (1H, dd, J = 8.3, 2.4 Hz, phenyl-H), 5.69 (1H, d, J = 14.6 Hz, ptb-triazole-CH$_2$-phenyl), 5.58 (1H, d, J = 14.6 Hz, ptb-triazole-CH$_2$-phenyl), 5.18 (1H, d, J = 14.6 Hz, ptb-triazole-CH$_2$-phenyl).

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NMR spectra were acquired on a Bruker Biospin AV400 spectrometer. $^1$H NMR spectra were acquired at 400 MHz, $^{13}$C($^1$H) NMR spectra were acquired at 100 MHz, and $^{15}$F NMR acquired at 376 MHz. All NMR spectra were recorded at 298 K. Chemical shifts were referenced to residual solvent peaks and are quoted in terms of parts per million (ppm), relative to tetramethylsilane (Si(CH$_3$)$_4$); $^{15}$F NMR signals are quoted relative to an internal standard of hexafluorobenzene.

[Ir(df-ppy)$_2$(ptb)](PF$_6$)$_4$: This complex was synthesised according to the previously published procedure.$^{26, 37}$ The $^1$H NMR spectrum (Fig. S13) was consistent with the literature values.$^{1}$ $^1$H NMR (400 MHz; CDCl$_3$); δ 8.80 (1H, s, ptb-triazolyl-H), 8.30 (2H, t, J = 10.5 Hz, phenyl-H), 8.22 (1H, d, J = 7.9 Hz, ptb-pyridyl-H), 8.00 (1H, td, J = 7.9, 1.5 Hz, ptb-pyridyl-H). 7.79-7.83 (3H, m, pyridyl-H, ptb-pyridyl-H), 7.61 (1H, d, J = 5.8 Hz, pyridyl-H), 7.45 (1H, d, J = 5.8 Hz, pyridyl-H), 7.36 (SH, s, ptb-phenyl-H), 7.32 (1H, m, pyridyl-H), 7.11 (1H, dd, J = 7.3, 5.9, 1.3 Hz, pyridyl-H), 7.01 (1H, dd, J = 7.3, 5.9, 1.3 Hz, pyridyl-H), 6.55 (2H, m, phenyl-H), 5.73 (1H, dd, J = 8.5, 2.5 Hz, phenyl-H), 5.68 (1H, dd, J = 8.5, 2.3 Hz, phenyl-H), 5.58 (2H, s, triazole-CH$_2$-phenyl). ESI-MS (positive ion). Calcd for C$_{35}$H$_{26}$F$_{12}$N$_{10}$P$_{4}$ ([M]$^+$): m/z 945.138. Found m/z 945.139.

Crystals of [Ir(df-ppy-CF$_3$)$_2$(ptb)](PF$_6$)$_4$ were mounted in low temperature oil then flash cooled. Intensity data were collected at 130.0(1) K on an X-ray diffractometer with CCD detector using MoK$_\alpha$ (λ = 0.71073 Å) radiation. The structure was solved by direct methods and difference Fourier synthesis.$^{34}$ Thermal ellipsoid plots were generated using the program ORTEP-3 integrated within the WINGX suite of programs.$^{35}$ Crystal data for [Ir(df-ppy-CF$_3$)$_2$(ptb)](PF$_6$)$_4$: Ir$_{39}$S$_{34}$C$_{98}$F$_{4}$I$_{26}$N$_{46}$P$_{4}$; M = 1714.71; T = 130.0(1) K; λ = 0.71073 Å; triclinic; space group P 1; a = 11.9028(4) Å; b = 12.475(4) Å; c = 14.8516(5) Å; α = 84.354(3)°; β = 77.044(3)°; γ = 75.899(3)°; V = 2077.80(13) Å$^3$; Z = 2; D$_c$ = 1.878 mg M$^{-3}$; μ(Mo Kα) = 3.491 mm$^{-1}$; F(000) = 1140; crystal size 0.562 × 0.148 × 0.044 mm$^3$; 19183 reflections measured; 12063 independent reflections (Rint = 0.0293); the final R = 0.0439 ([I > 2σ(I)]; wR$_2(F) = 0.1119$ (all data); GOOF = 1.032.

**Absorption and Photoluminescence Emission Spectra**

Absorption spectra were collected using Cary 300 Bio UV/Vis spectrophotometer (Agilent, Vic., Australia) with 1 cm path length Spectroslit Quartz fluorimeter cuvettes with screw-top caps (Starna, Vic., Australia). Room temperature...
photoluminescence spectra were collected using a Cary Eclipse spectrofluorimeter (5 nm band pass, 1 nm data interval, PMT voltage: 800 V; Agilent) with the cuvettes noted above. Low temperature photoluminescence spectra were obtained using an OptistatDN Variable Temperature Liquid Nitrogen Cryostat (Oxford Instruments, U.K.), with custom-made quartz sample holder (Fig. S17). Room temperature and low temperature emission spectra were corrected for the change in instrument sensitivity across the wavelength range, using a correction factor established using a quartz halogen tungsten lamp of standard spectral irradiance.

DFT calculations were carried out within the Gaussian 09 suite of programs. DFT calculations were carried out within the Gaussian 09 suite of programs.

Electrochemistry and ECL

The electrochemical cell comprised a cylindrical glass vessel with a flat base and custom-built Teflon lid with holes to fit the electrodes (glassy carbon working (CH Instruments), platinum wire counter and silver wire reference), and ensure a consistent cell configuration. The cell was housed in a light-tight faraday cage. Potentials were applied using an Autolab PGSTAT204 or PGSTAT128N potentiostat (Metrohm Autolab B.V., Netherlands), and referenced in situ to the ferrocene/ferrocenium (Fc/Fc’+) couple (0.2 mM). Spectra were collected using an Ocean Optics QE65pro or QEpro CCD spectrometer via optical fibre (1.0 m length, 1.0 mm core diameter) and collimating lens (Ocean Optics 74-UV, 200–2000 nm), positioned directly under the working electrode. Freshly distilled acetonitrile with 0.1 M TBAPF6 supporting electrolyte was used as the solvent. Prior to each experiment, each electrode was cleaned/polished. The working electrodes were polished using 0.3 mm and 0.05 mm alumina powder on a felt pad with deionised water. All electrodes were rinsed with acetonitrile or acetone and dried with either nitrogen or air.

The solvent was degassed with nitrogen or argon for 15 minutes. For sets of experiments in which the ECL intensity exceeded the range of the spectrometer under our normal conditions, the proportion of light reaching the spectrometer was lowered by reducing the entrance slit width. The ECL from multiple luminophores was deconvoluted into their characteristic spectral distributions using the Solver function of Microsoft Excel (e.g., Fig. S4).

Computational Methods

DFT calculations were carried out within the Gaussian 09 suite of programs. Ground state singlet and triplet geometries were optimised in the presence of solvent with the BP86 functional in conjunction with the def2-TZVP basis set and associated core potential. For Ir(ppy)3, the mPW1PW91 functional was used as geometry optimisation with BP86/def2-TZVP proved problematic. The polarisable continuum model (PCM) self-consistent reaction field (SCRF) was used to model solvent effects with Truhlar’s SMD solvent model, with a solvent of acetonitrile for consistency with the experimental system. Stationary points were characterised as minima by calculating the Hessian matrix analytically at the same level of theory. All structures are minima with no imaginary frequencies. Molecular orbitals were calculated at the BP86/def2-TZVP level of theory, which has previously been demonstrated to produce reliable results.

Molecular orbital analysis was carried out with the QMForge program.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


The annihilation electrogenerated chemiluminescence of mixtures of Ir(III) complexes is eliminated by manipulating reduction potentials through subtle changes in ligand structure.