

Extremely efficient electrochemiluminescence systems based on tris(2-phenylpyridine)iridium(III)

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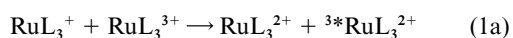
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Electron transfer generation of the excited tris(2-phenylpyridine)iridium(III) $^3\text{Ir}(\text{ppy})_3$ has been studied in acetonitrile–dioxane (1 : 1) solutions containing 0.1 M (*n*-C₄H₉)₄NPF₆ as the supporting electrolyte. A triple-potential-step technique was used to create electrochemiluminescence (ECL) emission by annihilation of the electrochemically generated ions $\text{Ir}(\text{ppy})_3^+ + \text{Ir}(\text{ppy})_3^-$ (single ECL system) as well as $\text{Ir}(\text{ppy})_3^+ + \text{A}^-$ (mixed ECL systems with the radical anions of aromatic nitriles and ketones). Very high ECL emission efficiencies (up to 0.67, close to the excited $^3\text{Ir}(\text{ppy})_3$ luminescence yield of 0.75) have been found.

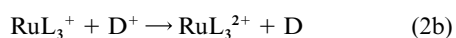
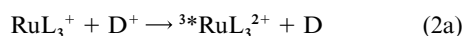
Introduction

Electrochemically generated chemiluminescence or electrochemiluminescence (ECL) can be defined as the generation of light by means of homogenous electron transfer reactions between precursors obtained as a consequence of electrode (heterogeneous) processes.^{1–5} Extensive investigations of ECL processes have established different ways for light emission occurring in ECL systems. Emitted photons can be directly produced by means of radiative electron transfer (ET) between oxidized and reduced reactant(s) or by emissive deactivation of the excited states populated in non-radiative ET processes. The emissive excited states may be directly formed in the ET process or in an up-conversion reaction (e.g. triplet–triplet annihilation) involving intermediate non-emissive excited states. Population of the lower lying non-emissive excited triplets seems to be the most important factor limiting ECL efficiencies in the cases of “pure” organic ECL systems.^{6–8}

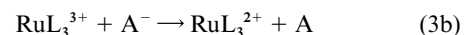
ECL systems involving luminescent transition metal complexes (e.g. phosphorescent 4d⁶ and 5d⁶ transition metal ion chelates with emission forced by the spin–orbit coupling) are relatively simple from the mechanistic point of view.^{9,10} They can be treated as a superposition of two ET reactions competitively leading to the population of the excited state (usually in the normal Marcus region with a low exothermicity ΔG_{es}) or to the ground state (in the inverted Marcus region with a high exothermicity ΔG_{gs}). Ruthenium(II) complexes RuL_3^{2+} , with the most noticeable and studied tris(2,2'-bipyridine)ruthenium(II) $\text{Ru}(\text{bipy})_3^{2+}$ ion, are typical examples with the reaction mechanism formulated as follows.^{11–21} In the electrochemical reactions the parent ions RuL_3^{2+} undergo one-electron reduction and oxidation to RuL_3^+ and RuL_3^{3+} species followed by ion's annihilation with the formation of the excited $^3\text{RuL}_3^{2+}$ state and subsequent emission of light:



Sufficiently low energy of the excited $^3\text{RuL}_3^{2+}$ states allows also for the experimental observation of ECL phenomenon in mixed systems, i.e., in the reactions between RuL_3^+ and strong oxidants or between RuL_3^{3+} and strong reductants.^{22–24} For example, ET reaction between stable radical cations D^+ and RuL_3^+ leads to a more or less efficient $^3\text{RuL}_3^{2+}$ generation:



In a similar way $^3\text{RuL}_3^{2+}$ generation may take place during ET reaction between RuL_3^{3+} and stable radical anions A^- :



Correspondingly, neutral organic radicals R^\cdot may be also applied as reducing agents, with the reaction scheme matching eqns. (3a) and (3b), but with R^\cdot and R^+ redox forms involved instead of A^- and A , respectively.

According to the above-presented reaction schemes, the ECL efficiencies ϕ_{ecl} are directly related to the yield of the excited state generation ϕ_{es} and to the emission quantum yield ϕ_{em} of a given emitter:

$$\phi_{\text{ecl}} = \phi_{\text{es}}\phi_{\text{em}} \quad (4)$$

The value of ECL efficiency ϕ_{ecl} (in photons emitted per electrons transferred between reduced and oxidized forms) was found to be 0.05 for the $\text{Ru}(\text{bipy})_3^{3+}/\text{Ru}(\text{bipy})_3^+$ ECL system in acetonitrile solutions at 25 °C. Since ϕ_{ecl} strictly approaches the intrinsic luminescence efficiency of the emitter ϕ_{em} (especially at lowered temperatures), it was concluded that the formation efficiency ϕ_{es} of the excited $^3\text{Ru}(\text{bipy})_3^{2+}$ upon reaction (1a) is near unity.¹⁶ Similar behavior was also observed for other RuL_3^{2+} complexes^{19–21} as well as for some mixed ECL systems involving the $\text{Ru}(\text{bipy})_3^{2+}$ ion^{22,24} indicating that the thermodynamically favored reactions to form directly the ground state product, are kinetically inhibited as compared with the excited product formation. More detailed and quantitative discussion of the ϕ_{ecl} value for a given ECL system may be done in terms of an ET model for chemiluminescence, first proposed by Marcus.²⁵

Results obtained for RuL_3^{2+} chelates strongly suggest that other transition metal complexes may be very useful in the search of new ECL systems with extremely high efficiencies. It is, however, a rather difficult task because of the required combination of high luminescence efficiency of the studied complex and stability of all redox species involved in the ET excitation. Further requirements of the solubility and chemical stability in the presence of electrodes, electrolyte and solvent as well as photochemical stability, additionally limit the number of the compounds suitable for ECL studies. Among many possible metal/ligand combinations, orthometallated iridium(III) complexes²⁶ show an interesting combination of photophysical and electrochemical properties, which makes them potentially useful in ECL studies. In particular, some Ir(III) complexes display promising luminescence properties – metal-to-ligand charge-

transfer phosphorescence (MLCT) – with very high emission efficiencies (in room temperature solutions) together with stability of the electrochemical reaction products.^{27–32} Therefore they seem to be promising candidates for ECL investigations. Demonstration^{32–35} of highly efficient green electrophosphorescence from Ir(III) derivatives as well as preliminary results from the ECL studies^{36–38} involving the tris(2-phenylpyridine)iridium(III) Ir(ppy)₃ complex furthermore maintain interest in fundamental and applied ECL research of these compounds.

In this paper we describe results from a more detailed study of Ir(ppy)₃-based electrochemiluminescence systems. We report the results of quantitative studies of ECL efficiency in the ions' recombination between the oxidized Ir(ppy)₃⁺ with the reduced Ir(ppy)₃⁻ or with strong organic reductants A⁻. Organic auxiliary acceptors A (aromatic nitriles and ketones) have been chosen because of (i) their A⁻ radical anions stability^{39,40} and (ii) relatively high energies of their excited (singlet ¹*A and triplet ³*A) states,⁴¹ higher than the excited ³*Ir(ppy)₃ energy (with $E_{MLCT} \approx 2.50$ eV).⁴² High energies of the organic ³*A triplets E_T , higher than E_{MLCT} , make their population an energetically less favorable process and exclude the excited ³*Ir(ppy)₃ quenching by means of energy transfer. The measurements have been performed in mixed acetonitrile–dioxane (1 : 1) solutions because Ir(ppy)₃ is only poorly soluble (~0.2 mM)³⁷ in pure acetonitrile.

Experimental

Materials

Uvasol quality toluene – TOL, acetonitrile – ACN (used as received) and 1,4-dioxane – DX (distilled over CaH₂) were obtained from Merck. Commercially available Ir(ppy)₃ – tris(2-phenylpyridine)iridium(III), was obtained from SynTec GmbH and used as received. Tris(2,2'-bipyridine)ruthenium(II) perchlorate, Ru(bipy)₃(ClO₄)₂, was synthesized using a procedure described in the literature⁴³ and purified by means of recrystallization from ACN–TOL mixtures. Samples of 4,4'-dicyanobiphenyl and 2-cyanofluorene or 4-acetylbiphenyl and 4-cyano-4'-methylbiphenyl were kindly received from Dr René Lapouyade (Bordeaux University) and Dr Jacek Nowacki (Warsaw University), respectively. Other organic compounds used were obtained from Sigma-Aldrich or Lancaster Synthesis. Tetrabutylammonium hexafluorophosphate was prepared by metathesis of (*n*-C₄H₉)₄NBr with KPF₆ in aqueous solution. The precipitated product was washed with water and recrystallized from HPLC grade methanol (Roth) and, before use, dried in a vacuum (at 100 °C) for 12 h. All, electrochemical and spectroscopic measurements were performed at room temperature (25 °C) in a mixed solvent (ACN–DX, 1 : 1 v/v, containing 0.1 M of the supporting electrolyte) deaerated with pure argon.

Spectroscopic instrumentation and procedures

Absorption spectra were recorded using a Shimadzu UV 2401PC spectrometer. Luminescence decays and luminescence spectra (corrected for the spectral sensitivity of the instrument) were measured by means of an Edinburgh Instruments FL900 fluorescence lifetime spectrometer or FS900 steady-state fluorometer, respectively. Luminescence decays (mono-exponential on the microsecond scale of observation) were analyzed by the single-curve method. Quinine sulfate in 0.05 M H₂SO₄ ($\phi_{em} = 0.51$)⁴⁴ and Ru(bipy)₃(ClO₄)₂ in ACN ($\phi_{em} = 0.06$)⁴⁵ served as the quantum yield standards for the luminescence quantum yield determinations.

Two quantum yield standards were used because our ϕ_{em} measurements gave values (0.70 and 0.75 in ACN and ACN–DX 1 : 1, respectively) distinctly higher than previously reported in TOL solutions (0.40).²⁸ Ru(bipy)₃²⁺ in oxygen-free

ACN was used as a secondary standard to verify the yields obtained against quinine sulfate. The data obtained were in excellent agreement (within an experimental error of 10%) against both standards used. The same results have been obtained using another, home-built 90° optical geometry fluorometer with a CDI2D-MPP CCD spectrograph (Control Development Inc.) applied as emission detector.

Electrochemical instrumentation and procedures

A home-built measurement setup^{7,23,46,47} was used for both electrochemical (cyclic voltammetry and coulometry) and electrochemiluminescence studies (ECL spectra and transients). The same electrochemical cell with the working electrode (a Pt disc with a diameter of 1 mm polished before each use with 1 μm diamond paste) was used for the electrochemical and ECL studies.

Cyclic voltammetry was run prior to the ECL measurements (to evaluate the electrochemical characteristics) as well as after ECL experiments (to check the temporal stability of the system studied). The cyclic voltammetry experiments allowed also to determine the redox potentials (referred to ferrocene–ferrocene⁺ (Fc/Fc⁺) internal reference redox couple) as well as the mean lifetime of the reactants involved in a particular ECL system.

The triple-step potential technique^{48,49} was used to create ECL emission recorded at 1 or 2 nm intervals from 350 to 850 nm. The experiment began with the working electrode at a potential of no electroactivity. At first the electrode potential was changed to values for the generation of the oxidant and subsequently to values corresponding to the formation of the reductant – sequence denoted as +/–. The potential limits of the program sequence were chosen so as to ensure production of the electrogenerated intermediates in the mass-transfer-controlled region and to minimize the influence of secondary electrochemical reactions. Subsequently, the electrode potential was again changed to the initial value. The system was allowed to equilibrate for a few seconds between each pulse sequence. The opposite sequence of the reactants generation, denoted as –/+ in which the reductant was generated first, has also been used. In both cases light emission was observed during the second reactant generation step in the course a triple-potential-step sequence. The ECL spectra obtained were integrated to obtain the total photon intensities. The values of the measured integrated photon intensities were the averages of several independent measurements. For a particular solution, a few measurements were made to check the temporal stability of the system studied. ECL yields were determined against the standard (ECL system containing 1 mM of Ru(bipy)₃²⁺ in 0.1 M (C₂H₅)₄NPF₆/ACN with $\phi_{ecl} = 0.05$)¹⁶ by comparison of the measured integrated photon intensities, taking into account the differences in the electric charges passed through the solution studied. The error of ϕ_{ecl} determination was estimated to be 10–15%.

Results and discussion

Electrochemistry

The cyclic voltammogram recorded for 1 mM Ir(ppy)₃ in an ACN–DX 1 : 1 mixture (Fig. 1) shows three one-electron processes. Similarly, as was previously reported for ACN or tetrahydrofuran solutions, the Ir(ppy)₃ complex can be oxidized and reduced to the corresponding stable Ir(ppy)₃⁺ (at $E_{ox} = +0.31$ V vs. Fc/Fc⁺) and Ir(ppy)₃⁻ (at $E_{red} = -2.70$ V) species. Ir(ppy)₃⁻ can be further reduced to stable Ir(ppy)₃²⁻ (at $E_{red} = -2.95$ V):

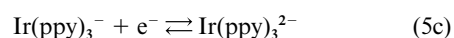
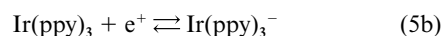
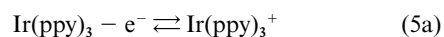


Table 1 Redox potentials (E_{red}), standard free energies for the ground (ΔG_{gs}) and excited state (ΔG_{es}) population and ECL efficiencies (ϕ_{ECL}) for the $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ systems studied (room temperature data for acetonitrile–dioxane 1 : 1 solutions containing 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte)

| Acceptor | $E_{\text{red}}^a/\text{V}$ | $\Delta G_{\text{gs}}^b/\text{eV}$ | $\Delta G_{\text{es}}^c/\text{eV}$ | ϕ_{ECL} |
|-----------------------------------|-----------------------------|------------------------------------|------------------------------------|--------------------------|
| 2-Cyanofluorene | -2.55 | -2.86 | -0.36 | 0.67 |
| 4-Cyano-4'-methylbiphenyl | -2.51 | -2.82 | -0.32 | 0.59 |
| 4-Cyanobiphenyl | -2.47 | -2.78 | -0.28 | 0.62 |
| 2-Cyanonaphthalene | -2.46 | -2.77 | -0.27 | 0.29 |
| 1-Cyanonaphthalene | -2.34 | -2.65 | -0.15 | 0.36 |
| 4-Acetylbiphenyl | -2.33 | -2.64 | -0.14 | 0.26 |
| 2-Acetylnaphthalene | -2.32 | -2.63 | -0.13 | 0.37 |
| 9-Cyanophenanthrene | -2.29 | -2.60 | -0.10 | 0.33 |
| 1-Acetylnaphthalene | -2.26 | -2.57 | -0.07 | 0.30 |
| Benzophenone | -2.24 | -2.55 | -0.05 | 0.25 |
| 1,2-Dicyanobenzene | -2.13 | -2.44 | +0.06 | 0.20 |
| 4,4'-Dicyanobiphenyl | -2.12 | -2.43 | +0.07 | 0.23 |
| 4-Cyanobenzoic acid methyl ester | -2.10 | -2.41 | +0.09 | 3.7×10^{-2} |
| 4-Acetylbenzoic acid methyl ester | -2.04 | -2.35 | +0.15 | 6.0×10^{-4} |
| 1,4-Dicyanobenzene | -2.03 | -2.34 | +0.16 | 2.2×10^{-3} |
| 4-Acetylbenzotrile | -1.96 | -2.27 | +0.23 | 4.0×10^{-5} |
| 4-Acetylacetophenone | -1.95 | -2.26 | +0.24 | 1.7×10^{-5} |
| 1,4-Dicyanonaphthalene | -1.73 | -2.04 | +0.46 | No emission ^d |

^a Redox potential for A/A^- couple according to the Fc/Fc^+ internal reference redox system. ^b Values calculated according to eqn. (10a) with the redox potential of $\text{Ir}(\text{ppy})_3/\text{Ir}(\text{ppy})_3^+$ couple $E_{\text{ox}} = +0.31$ V vs. Fc/Fc^+ . ^c Values calculated according to eqn. (10b) with the $^3\text{Ir}(\text{ppy})_3$ excited state energy $E_{\text{MLCT}} = 2.50$ eV. ^d The sensitivity threshold of the photon detection part of our ECL equipment was about 10^{-7}

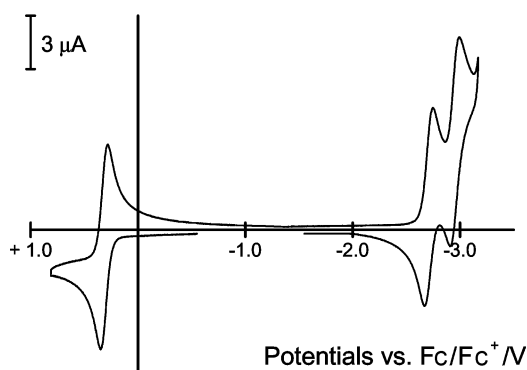


Fig. 1 Cyclic voltammogram (recorded at Pt electrode with scan rate $V_p = 100$ mV s^{-1}) of 1 mM $\text{Ir}(\text{ppy})_3$ in acetonitrile–dioxane 1 : 1 solutions containing 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte. Potential scale according to the internal Fc/Fc^+ reference redox system.

The above processes are electrochemically reversible according to anodic/cathodic peak separations ΔE_p (ca. 60 mV at scan rate $V_p = 100$ mV s^{-1}). A third reduction wave, corresponding to $\text{Ir}(\text{ppy})_3^{3-}$ formation (with $E_{\text{red}} = -3.19$ V reported for tetrahydrofuran solutions³⁵) could not be observed under our experimental conditions, because of the redox potential value being more negative than the solvent cathodic limit.

The cyclic voltammograms recorded in solutions containing additionally 1 mM of organic co-reactant show, at potentials less negative than $\text{Ir}(\text{ppy})_3/\text{Ir}(\text{ppy})_3^-$ couple, an additional peak system corresponding to reversible ($\Delta E_p = 60\text{--}70$ mV) or quasi-reversible ($\Delta E_p = 80\text{--}120$ mV) reduction of the neutral molecules A to their radical anions A^- .



Measured values of the $E_{\text{red}}(\text{A}/\text{A}^-)$ values are collected in Table 1. Stable radical anions A^- can be further reduced (usually irreversibly to unstable products) at more negative potentials overlapping the reduction of $\text{Ir}(\text{ppy})_3$.

The potential–current curves recorded at $V_p = 100$ mV s^{-1} had a peak current on the reverse sweeps approximately equal to that for the forward sweeps, indicating that the redox species studied (i.e., $\text{Ir}(\text{ppy})_3^+$, $\text{Ir}(\text{ppy})_3^-$ and A^- ions) are quite stable.

The cyclic voltammetry experiments allowed us to determine that their mean lifetimes lie in the range of seconds. Because the time of ECL experiments was usually 100 ms, complications caused by the ECL reactants instabilities may be ruled out.

ECL spectra and transients

The application of a triple-potential sequence causes emission, characteristic for the excited $^3\text{Ir}(\text{ppy})_3$ luminescence, to appear in the single $\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3^-$ as well as in the mixed $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ ECL systems. Within the experimental error the ECL emission bands (shown in Fig. 2) agree well with those observed with photoexcitation.

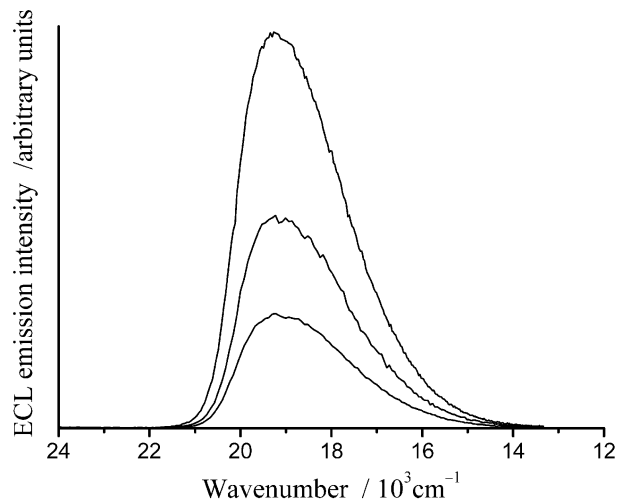


Fig. 2 ECL spectra of the mixed $\text{Ir}(\text{ppy})_3^+/\text{2-cyanofluorene}^-$, $\text{Ir}(\text{ppy})_3^+/\text{1-cyanonaphthalene}^-$ and $\text{Ir}(\text{ppy})_3^+/\text{1,2-dicyanobenzene}^-$ systems (from top to bottom) in acetonitrile–dioxane 1 : 1 solutions containing 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte. The presented spectra (recorded in solutions containing $\text{Ir}(\text{ppy})_3$ and organic co-reactant in 1 mM concentration) are normalized to reproduce the relative ECL intensities for the system studied.

Analyses of the ECL transients have been performed using the relationship between $I(\Delta t_R)$ and the time delay, Δt_R , from the start of the second, reverse potential step (with the duration time t_R) in the triple-potential-step experiments.^{48,49} In the cases

of the mixed $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ ECL systems $I(\Delta t_R)$ transients can be linearized according to so-called Feldberg plot:

$$I(\Delta t_R) = a \sqrt{\frac{t_F}{\Delta t_R}} - b \quad (7)$$

Experimental values of slope-to-intercept ratios have been found to be close to the theoretical value of 0.959 (some representative examples are shown in Fig. 3), pointing to direct formation of the emitting ${}^3\text{Ir}(\text{ppy})_3$ in the annihilation of $\text{Ir}(\text{ppy})_3^+$ and A^- ions:

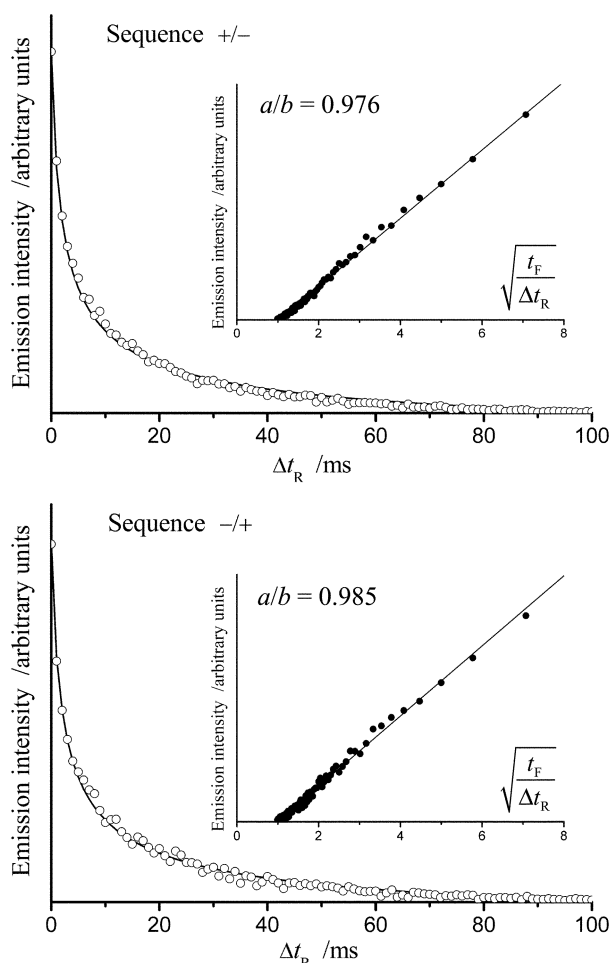
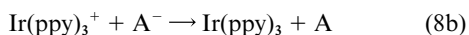
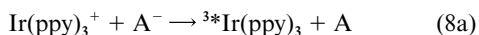
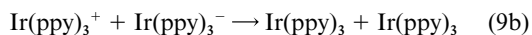
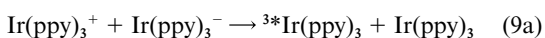


Fig. 3 ECL decay curves and plots of intensities $I(\Delta t_R)$ vs. $(t_F/\Delta t_R)^{1/2}$ recorded for the mixed $\text{Ir}(\text{ppy})_3^+/\text{benzophenone}^-$ system in acetonitrile-dioxane 1 : 1 solutions containing 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte and 1 mM of $\text{Ir}(\text{ppy})_3$ and benzophenone. Sequences $-/+$ and $+/-$ denote the order of the reactant generations (first reductant or first oxidant, respectively). Forward and reverse pulse duration times (t_F and t_R , correspondingly) were 100 ms for both cases.



Most likely the same mechanism is also appropriate for the case of single $\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3^-$ ECL system:



where, however, intrinsic deviation from linearity in the Feldberg plots have been found (Fig. 4). During the second, reverse step in the triple-potential-step experiments ECL emission intensity drops distinctly faster than expected, suggesting the

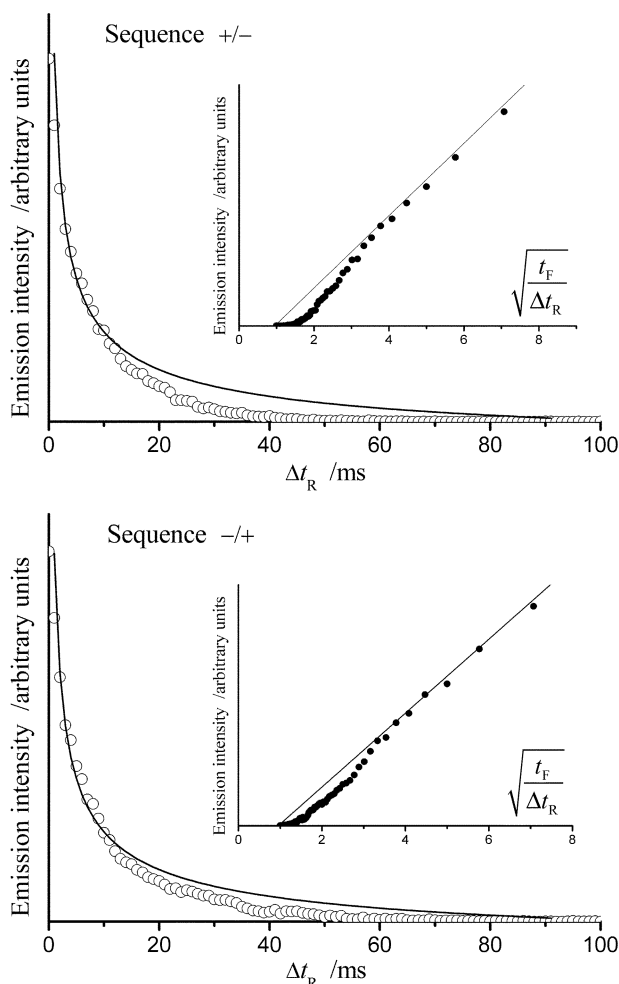


Fig. 4 ECL decay curves and plots of intensities $I(\Delta t_R)$ vs. $(t_F/\Delta t_R)^{1/2}$ recorded for the single $\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3^-$ system in acetonitrile-dioxane 1 : 1 solutions containing 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte and 1 mM of $\text{Ir}(\text{ppy})_3$. Sequences $-/+$ and $+/-$ denote the order of the reactant generations (first reductant or first oxidant, respectively). Forward and reverse pulse duration times (t_F and t_R , correspondingly) were 100 ms for both cases.

presence of some additional parasitic processes, probably connected with the very negative reduction potential of $\text{Ir}(\text{ppy})_3$. No attempts were made to determine the nature of the interfering processes, but it is very probable that partial reduction of the supporting electrolyte $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cation and/or solvent(s) molecules (as already pointed in ref. 37) may be responsible for the observed behavior. Under conditions where the $\text{Ir}(\text{ppy})_3$ reduction is near the solvent cathodic limit, another produced species may act as an effective ${}^3\text{Ir}(\text{ppy})_3$ quencher or/and may be involved in ET reactions with $\text{Ir}(\text{ppy})_3^+$ ion.

ECL efficiencies – experimental values

The functional dependence of ϕ_{ecl} on the ET exergonicity has been observed in the cases of the mixed $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ ECL systems, as expected and found previously for other ECL systems.^{8,22,24,50} The value of ϕ_{ecl} rapidly increases and approaches a quasi-plateau (Fig. 5) with the increase of the absolute value of the Gibbs free energy of the $\text{Ir}(\text{ppy})_3^+$ and A^- ions' recombination ΔG_{gs} (or correspondingly ΔG_{es}) given by the difference between the oxidation and reduction potentials:

$$\Delta G_{\text{gs}} = F(E_{\text{red}} - E_{\text{ox}}) \quad (10a)$$

$$\Delta G_{\text{es}} = F(E_{\text{red}} - E_{\text{ox}}) + E_{\text{MLCT}} \quad (10b)$$

where F is the Faraday constant. Extremely high (0.59–0.67) at sufficiently negative ($\Delta G_{\text{es}} < -0.25$ eV) values have been

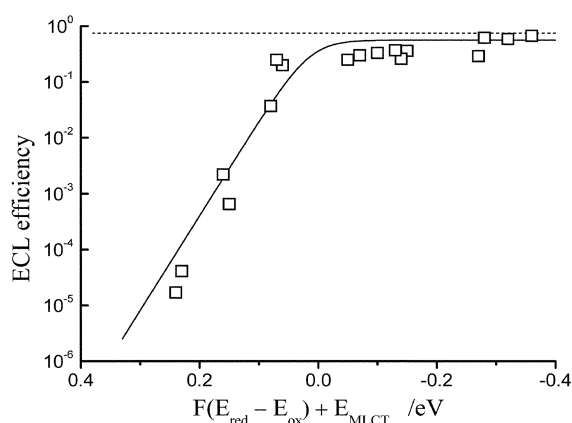


Fig. 5 Plot of $\log(\phi_{\text{ecl}})$ vs. ΔG_{es} (the Gibbs free energy of the excited state formation) for the mixed $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ ECL systems (measured for 1 mM of $\text{Ir}(\text{ppy})_3$ and organic co-reactant in 1 mM concentration in acetonitrile–dioxane 1 : 1 solutions containing 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte). The dotted horizontal line corresponds to the emission quantum yield of the excited ${}^3\text{Ir}(\text{ppy})_3$.

observed. Generated ECL emission was intense enough to be observed in a daily-lighted laboratory room. In our, somewhat arbitrary opinion, the generated light from the ECL cell was distinctly brighter than from the LED indicators on the front panels of our ECL equipment. Relatively low ϕ_{ecl} efficiencies (below 10^{-2}) for ΔG_{es} more positive than +0.10 eV and no (below 10^{-7}) emission at $\Delta G_{\text{es}} = +0.46$ eV (for the $\text{Ir}(\text{ppy})_3^+/\text{1,4-dicyanobenzene}^-$ system), as expected, were found.

In the case of the single $\text{Ir}(\text{ppy})_3^+/\text{Ir}(\text{ppy})_3^-$ ECL system, with maximally negative $\Delta G_{\text{es}} = -0.51$ eV, somewhat smaller ϕ_{ecl} efficiencies, *ca.* 0.16, have been found (at $t_{\text{F}} = t_{\text{R}} = 100$ ms), in good agreement with that determined in ACN solutions (0.14).³⁷ Most probably, it is caused by presence of additional parasitic processes (responsible also for the non-linearity observed in the recorded ECL transients) occurring during electrochemical excitation. It is of note that similar effects are not observed for ruthenium(II) complexes, which may be explained by less negative (by *ca.* 1 V) redox potentials of $\text{RuL}_3^{2+}/\text{RuL}_3^+$ pairs.^{22,24}

The very high ECL yields found clearly establish that the emitting ${}^3\text{Ir}(\text{ppy})_3$ state is also formed with high ϕ_{es} efficiencies. With the quantum efficiency $\phi_{\text{em}} = 0.75$ one can simply (eqn. (4)) obtain ϕ_{es} values close (within the experimental errors) to unity for the most efficient ECL systems studied in this work, similarly as found for ECL systems based on $\text{Ru}(\text{bipy})_3^{2+}$.^{16,22,24} For positive ΔG_{es} values, however, ϕ_{es} efficiencies found for $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ systems are one to two orders of magnitude larger than those found for $\text{Ru}(\text{bipy})_3^{3+}/\text{A}^-$ or $\text{Ru}(\text{bipy})_3^+/\text{D}^+$ pairs.^{22,24} (at the same ΔG_{es}). Evidently, the kinetic inhibition of the direct ground-state product formation is more pronounced in the case of $\text{Ir}(\text{ppy})_3$ than for $\text{Ru}(\text{bipy})_3^{2+}$.

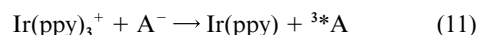
Electron-transfer excitation mechanism

More detailed and quantitative discussion of the ϕ_{ecl} or ϕ_{es} values may be done in terms of the above-mentioned Marcus model.²⁵ ET between oxidized and reduced reactants leads competitively to the population of the excited state (low exergonic reactions (8a) and (9a)) or to the ground state (high exergonic reactions (8b) and (9b)). Simple superposition of the two ET channels, however, is somewhat oversimplified from the mechanistic point of view. In real cases, both ET processes are preceded and followed by the diffusion of reactants and products from/into the bulk solution. Moreover, ECL reactants and products are species with distinctly different spin multiplicities, which causes an additional kinetic complication because of spin conservation rules.

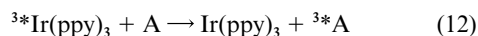
In the case of the $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ ECL systems a plausible reaction mechanism can be formulated as presented in Fig. 6. The electrochemically generated, oxidized $\text{Ir}(\text{ppy})_3^+$ and the reduced

A^- species form (in a diffusion controlled process) an activated complex (presumably a contact ion pair) in two different spin states with (according to the spin statistic rule^{51,52}) a branching ratio of 3 : 1. Generation of ${}^3\text{Ir}(\text{ppy})_3$ species from the triplet ${}^3[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+]$ precursor is much more efficient with respect to the singlet ${}^1[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+]$ one, because ET within the activated complex in the triplet state ${}^3[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+]$ leads directly (with rate k_{R}) to excited ${}^3\text{Ir}(\text{ppy})_3$ generation. Correspondingly, the triplet–singlet up-conversion (${}^3[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+] \rightarrow {}^1[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+]$ with rate k_{TS}) is a necessary step before the electron transfer to the ground state product. An activated complex in the singlet state ${}^1[\text{Ir}(\text{ppy})_3^+ \cdots \text{A}^-]$ exhibits exactly opposite behavior. Electron transfer leads directly to the ground state products (with rate k_{R}) but the excited ${}^3\text{Ir}(\text{ppy})_3$ formation is preceded by singlet–triplet up-conversion (with rate k_{ST}). Taking into account presumably very small energy splitting between two spin forms of the activated complex one can also assume that $3k_{\text{ST}} \approx k_{\text{TS}}$.

Excited state generation of the organic co-reactants is not included in the kinetic scheme because their energies E_{T} are high and their population is an energetically unfavorable process. Energies E_{T} higher than E_{MLCT} preclude also efficient quenching of the ${}^3\text{Ir}(\text{ppy})_3$ excited state by means of energy transfer. For organic co-reactants with E_{T} lower than E_{MLCT} , however, both the processes may play an important role. Preliminary results from our studies concerning organic co-reactants with low lying lowest excited triplets ${}^3\text{A}$, *e.g.*, the $\text{Ir}(\text{ppy})_3^+/\text{anthracene}^-$ system, agree well with the anticipated pattern. Despite high exothermicity of this particular ECL system ($\Delta G_{\text{es}} = -0.24$ eV) the obtained ECL efficiency, $\phi_{\text{ecl}} = 1.8 \times 10^{-3}$, is rather low, lower by a factor ~ 200 than found for other organic co-reactants with similar ΔG_{es} . The low energy of the anthracene triplet $E_{\text{T}} = 1.8$ eV⁴¹ allows the efficient generation of ${}^3\text{A}$:



as well as the energy transfer quenching:



Taking into account the excited ${}^3\text{Ir}(\text{ppy})_3$ lifetime ($\tau_{\text{L}} = 1.8$ μs in ACN–DX) and the maximal applied concentration of the anthracene quencher ($C_{\text{Q}} = 10^{-3}$ M) one can estimate the quenching process efficiency using the Stern–Volmer approach:⁵³

$$\frac{I_{\text{Q}}}{I} = \frac{1}{1 + k_{\text{Q}}\tau_{\text{L}}C_{\text{Q}}} \quad (13)$$

where I and I_{Q} are the emission intensities in the absence or presence of quencher. With the assumption of the quenching process occurring with a diffusion controlled rate ($k_{\text{Q}} \approx 10^{10}$ $\text{M}^{-1} \text{s}^{-1}$), the obtained value of $k_{\text{Q}}\tau_{\text{L}}C_{\text{Q}} \approx 18$ allows us to conclude that both processes can be operative. More detailed investigations performed for organic co-reactants with different E_{T} energies are necessary to give a decisive answer which process is more important.

ECL efficiencies – theoretical predictions

The proposed kinetic scheme for the ET generation of excited ${}^3\text{Ir}(\text{ppy})_3$ can be solved using the steady-state approximation:^{23,24}

$$\frac{\phi_{\text{es}}}{1 - \phi_{\text{es}}} = \frac{k_{\text{sep}}k_{\text{R}}/(k_{\text{sep}} + k_{\text{bt}})}{k_{\text{R}}} \times \frac{3(k_{\text{dis}} + 4k_{\text{TS}} + k_{\text{R}})}{(k_{\text{dis}} + 4k_{\text{TS}} + k_{\text{sep}}k_{\text{R}}/(k_{\text{sep}} + k_{\text{bt}}))} \quad (14)$$

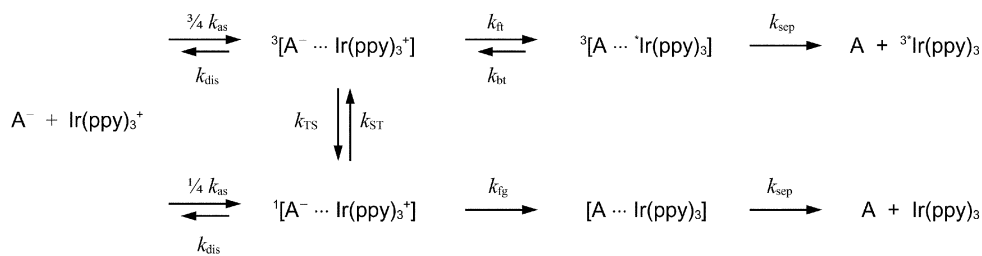


Fig. 6 Reaction mechanism for the excited ${}^3\text{Ir}(\text{ppy})_3$ generation in the reductive $\text{Ir}(\text{ppy})_3^+ + \text{A}^-$ ions' recombination processes.

where the $k_{\text{sep}}k_{\text{ft}}/(k_{\text{sep}} + k_{\text{bt}})$ term (an "effective rate" of the excited state population) takes also into account diffusion-controlled separation of the ET product ${}^3[\text{A}^- \cdots \text{Ir}(\text{ppy})_3]$ into the bulk solution. The obtained relationship is quite complex and rather difficult to use without additional information about the elementary rates involved in the overall reaction scheme. Some additional (somewhat arbitrary) assumptions are necessary before eqn. (14) can be applied to interpret the experimental ϕ_{es} values. These include an assumption of very slow spin up-conversion processes and very fast ET events (as compared to the diffusional limitation) which leads to a much simpler expression:

$$\frac{\phi_{\text{es}}}{1 - \phi_{\text{es}}} = 3 \frac{k_{\text{sep}}k_{\text{ft}}/k_{\text{dis}}k_{\text{bt}}}{1 + k_{\text{sep}}k_{\text{ft}}/k_{\text{dis}}k_{\text{bt}}} = \frac{3}{1 + k_{\text{dis}}k_{\text{bt}}/k_{\text{sep}}k_{\text{ft}}} \quad (15)$$

Both $k_{\text{dis}}/k_{\text{sep}}$ and $k_{\text{bt}}/k_{\text{ft}}$ terms can be easily estimated. Applying a familiar Einstein–Smoluchowski equation⁵⁴ the $k_{\text{dis}}/k_{\text{sep}}$ ratio can be expressed as:

$$\frac{k_{\text{dis}}}{k_{\text{sep}}} = \frac{w_{\text{R}}/RT}{1 - \exp(-w_{\text{R}}/RT)} \quad (16)$$

where w_{R} , R , T are the electrostatic attraction term between oppositely charged $\text{Ir}(\text{ppy})_3^+$ and A^- ions, the gas constant and the absolute temperature, respectively. Correspondingly k_{bt} and k_{ft} ET rate constants are connected by:

$$\frac{k_{\text{bt}}}{k_{\text{ft}}} = \exp\left[\frac{\Delta G_{\text{es}} - w_{\text{R}}}{RT}\right] \quad (17)$$

Combination of eqns. (15)–(17) and (4) leads simply to the final relationship between ϕ_{ecl} and ΔG_{es} quantities:

$$\phi_{\text{es}} = \frac{3}{4} \phi_{\text{em}} \times \frac{1}{1 + \frac{1}{4} \times (w_{\text{R}}/RT)/[\exp(w_{\text{R}}/RT) - 1] \exp(\Delta G_{\text{es}}/RT)} \quad (18)$$

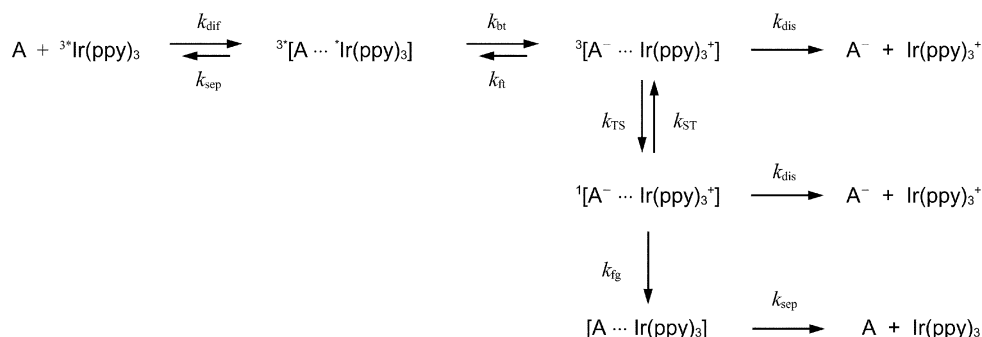


Fig. 7 Reaction mechanism for the oxidative electron transfer quenching of excited ${}^3\text{Ir}(\text{ppy})_3$.

Using experimental values of ΔG_{es} (as calculated from eqn. (10b)) ϕ_{ecl} efficiencies can be straightforwardly predicted with an appropriate w_{R} term estimated using the ordinary Coulomb equation or more sophisticated (and more applicable for solutions containing supporting electrolyte) Debye^{55,56} equations. With the dielectric constant $\epsilon \approx 25$ (as obtained from the Onsager relation⁵⁷ between ϵ and the concentration of the permanent dipole molecules in the ACN–DX mixture) and the $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ separation distance $d \approx 0.8$ – 1.0 nm (as obtained from the molar radii of $\text{Ir}(\text{ppy})_3$ and A molecules) the calculated w_{R} values are -0.07 and -0.02 eV, respectively. The value calculated for the Debye-limiting case ($w_{\text{R}} = -0.02$ eV) may be somewhat underestimated because of the assumption that the $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ supporting electrolyte is fully dissociated in the ACN–DX solution. It should be noted, however, that the $\zeta = 0.25 \times (w_{\text{R}}/RT)/[\exp(w_{\text{R}}/RT) - 1]$ term in eqn. (18) is only slightly sensitive to w_{R} ($\zeta = 0.25$ for $w_{\text{R}} = 0$ eV and $\zeta = 2.5$ for $w_{\text{R}} = -0.25$ eV, respectively). The corresponding values of $\zeta = 0.36$ and 0.73 have been calculated for $w_{\text{R}} = -0.02$ and -0.07 eV.

The solid line in Fig. 5 corresponds to ϕ_{ecl} values calculated with an intermediate value of ζ (0.57). Taking into account all simplifications in the approach applied the obtained agreement between theory and experiment can be regarded as satisfactory. It seems that the $\text{Ir}(\text{ppy})_3^+/\text{A}^-$ ECL systems studied indeed approximately correspond to the diffusion-limited case, contrary to the $\text{Ru}(\text{bipy})_3^{3+}/\text{A}^-$ or $\text{Ru}(\text{bipy})^+/\text{D}^+$ ECL systems, where kinetic limitations of k_{ft} and k_{TS} rates take place.^{22–24} This remains, however, only a very plausible hypothesis until the ET reactions involving the excited ${}^3\text{Ir}(\text{ppy})_3$ complex are better understood. More detailed investigation of the ET quenching processes (most probably occurring according to the scheme presented in Fig. 7) can lead to a decisive answer. Results from the ${}^3\text{Ir}(\text{ppy})_3$ quenching studies can also explain observed deviations from the expected, strictly monotonic relationship between ϕ_{ecl} and ΔG_{es} . Especially, transient absorption data (ions' separation efficiencies) are necessary to verify the assumed very slow ($k_{\text{dis}} \gg k_{\text{TS}}$) spin up-conversion between the singlet ${}^1[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+]$ and the triplet ${}^3[\text{A}^- \cdots \text{Ir}(\text{ppy})_3^+]$ forms of the activated complex.

Conclusions

The presented results undoubtedly show a possibility to design new extremely efficient electrochemiluminescence (ECL) systems based on tris(2-phenylpyridine)iridium(III), Ir(ppy)₃. The stability of both reagents, the oxidized form of Ir(ppy)₃ and the reduced form of organic co-reactant A in the mixed ECL system, with the direct population of the excited strongly emissive ³*Ir(ppy)₃ state with a high yield simplify the ECL experiments and their interpretation. The obtained ECL efficiency, 0.67 for the Ir(ppy)₃⁺/2-cyanofluorene⁻ system is, to the best our knowledge, the highest efficiency reported.

Ir(III) complexes seem to be very promising materials for further more detailed ECL investigations. In view of their electrochemical and spectroscopic properties one can expect that ECL mechanism will be similar to that found for Ir(ppy)₃, similarly as is in the case for different ruthenium(II) chelates. The fact that Ir(III) chelates emit over a range of wavelengths allows to design efficient multicolor ECL systems, which may be important from a practical point of view. On the other hand, ECL systems based on Ir(III) complexes offer also a useful approach to the study of very exergonic bimolecular electron-transfer reactions.

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