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Electrochemiluminescence studies of the cyclometalated iridium(III) complexes with substituted 2-phenylbenzothiazole ligands

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Abstract

Electrogenerated chemiluminescence (ECL) studies have been performed for the iridium(III) cyclometalated $L_2Ir(acac)$ complexes with substituted 2-phenylbenzothiazole ligand L. Electron transfer (ET) generation of the excited $^{3*}L_2Ir(acac)$ has been studied using a triple-potential-step technique in acetonitrile–dioxane (1:1) solutions containing 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ as the supporting electrolyte. ET reactions between electrochemically generated $L_2Ir(acac)^+$ and A^- (radical anions of aromatic nitriles) species lead to very efficient generation of ECL emission. Extremely high ECL efficiencies (up to 0.40) close to the excited $^{3*}L_2Ir(acac)$ luminescence yields have been found.

Keywords: Electrogenerated chemiluminescence; Iridium complexes; MLCT excited state

1. Introduction

Among many luminescent d^6 metal complexes the iridium(III) cyclometalated derivatives with very large photoluminescence efficiencies have recently attracted considerable attention as the emissive dopants in the organic light-emitting diode (OLED) devices [1–5]. Orthometalating ligands like 2-phenylpyridine and their substituted derivatives [6,7] strongly enhance electron density at the metal core (due to σ-donation through the metal–carbon bond), affecting significantly the physicochemical properties of Ir(III) complexes. It is especially true for the metal-to-ligand charge-transfer (MLCT) excited states, which allows fine tuning of their luminescence properties by a proper selection of the ligands [8–10].

Iridium(III) complexes seem to be also very promising materials for the electricity-to-light conversion in the electrogenerated chemiluminescence (ECL) reactions [11–16]. Electron transfer processes occurring between electrochemically generated precursors, e.g., between the oxidized form of tris(2-phenylpyridine)iridium(III) $Ir(ppy)_3^+$ and the reduced form of organic co-reactant A^-

$$Ir(ppy)_3^+ + A^- \rightarrow {}^{3*}Ir(ppy)_3 + A \qquad (1)$$

allow the direct population of the excited strongly emissive $^{3*}Ir(ppy)_3$ with a high yield (up to 0.67 for $Ir(ppy)_3^+$/2-cyanofluorene$^-$ system) [15]. The value of 0.67 is, to the best our knowledge, the highest ECL efficiency reported.

Extremely high ECL efficiencies ϕ_{ecl} (expressed in number of photons emitted per number of electron transferred) reported for $Ir(ppy)_3$ complex [15] undoubtedly show a possibility to design new efficient ECL systems based on iridium(III) chelates. This possibility is additionally attractive because Ir(III) cyclometalated complexes emit very efficiently over a wide range of

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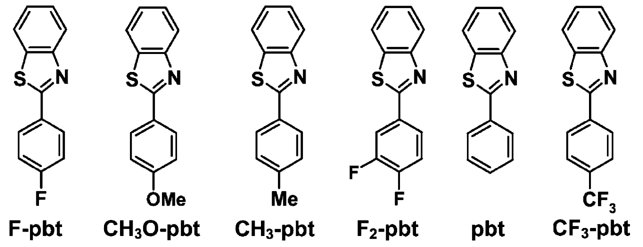

Fig. 1. Structural formulae of the ligands studied and their acronyms used in the text. N and C_2' are the chelating atoms.

wavelengths. It affords opportunity to design efficient multicolor ECL system, which may be important from a practical point of view.

In this communication, we describe investigation of the ECL systems based on Ir(III) chelates (neutral complexes of the general formula $L_2Ir(acac)$, where acac is the acetylacetone anion) with 2-phenyl-benzothiazole derivatives (see Fig. 1). We report, the results of quantitative studies of ECL efficiency in the ions' recombination between $L_2Ir(acac)^+$ with strong organic reductants A^- (radical anions of 1,4-dicyanonaphthalene (DCN), 4-acetylbenzonitrile (ABN) and 1,4-dicyanobenzene (DCB).

2. Experimental

The investigated complexes were synthesized and purified as described previously [17]. $(F_2\text{-pbt})_2Ir(acac)$ complex, until yet not described in the literature, has been prepared in the same way as described for $(pbt)_2Ir(acac)$ using 2-(3,4-difluorophenyl)benzothiazole ligand obtained by the condensation of 3,4-difluorobenzoyl chloride with 2-amino-thiophenol in *N*-methylpyrrolidone solutions. Spectroscopic grade solvent acetonitrile (ACN) (used as received) and 1,4-dioxane (DX) (distilled over CaH_2) were purchased from Sigma–Aldrich. The mixture ACN–DX (1:1 v,v) was used in the reported investigation because of somewhat limited solubility of $L_2Ir(acac)$ complexes with fluorine containing ligands in pure ACN. Moreover, it has been found that addition of DX distinctly improves reproducibility and efficiency of the ECL system studied. Tetrabutylammonium hexafluorophosphate $TBAPF_6$ (used as supporting electrolyte) was prepared by metathesis of $(n\text{-}C_4H_9)_4NBr$ with KPF_6 in aqueous solutions. The precipitated product was recrystallized form HPLC grade methanol (Roth) and, before use, dried in vacuum (at 100 °C) for 12 h. All, spectroscopic and electrochemical investigations were performed at room temperature (20 °C) in a mixed solvent deaerated with pure argon.

A home-built measurements setup (described previously in [18–20]) was used for both electrochemical and ECL studies performed in solutions containing 0.1 M of the supporting electrolyte and 1 mM of the electroactive species, respectively. The triple-step potential technique [21,22] was used to create ECL emission recorded at 1 or 2 nm intervals from 450 to 800 nm. The ECL efficiencies were determined against the standard (ECL system containing 1 mM of $Ru(2,2'\text{-bipyridine})_3^{2+}$ in ACN solutions with $\phi_{ecl} = 0.05$) [23] by comparison of the measured integrated photon intensities, taking into account the differences in electric charges passed through solutions. The error of ϕ_{ecl} determination was estimated to be 10–15%.

Luminescence spectra were measured by means of an Edinburgh Instruments FS900 steady-state fluorimeter. Luminescence quantum yields of the studied complexes ϕ_{em} were determined (with an error ca. 5–10%) against quinine sulfate in 0.05 M H_2SO_4 with $\phi_{em} = 0.51$ [24].

3. Results and discussion

Cyclic voltammetry was run prior to the ECL measurements to evaluate the electrochemical characteristics and after ECL experiments to check the temporal stability of the system studied. The cyclic voltammograms recorded for 1 mM $L_2Ir(acac)$ in an ACN–DX mixture show reversible processes corresponding to one-electron oxidation and one-electron reduction:

$$L_2Ir(acac) - e^- \leftrightharpoons L_2Ir(acac)^+ \tag{2}$$

$$L_2Ir(acac) + e^- \leftrightharpoons L_2Ir(acac)^- \tag{3}$$

$L_2Ir(acac)^-$ anions can be further reduced to less stable $L_2Ir(acac)^{2-}$ species. The cyclic voltammograms recorded in solutions containing additionally 1 mM of organic co-reactant show, at potential less negative than $L_2Ir(acac)/L_2Ir(acac)^-$ couple, an additional peak system corresponding to reversible reduction of the neutral molecules A to their radical anion A^- (see Fig. 2)

$$A + e^- \leftrightharpoons A^- \tag{4}$$

The measured values of the E_{ox} and E_{red} potentials for $L_2Ir(acac)/L_2Ir(acac)^+$ and $L_2Ir(acac)/L_2Ir(acac)^-$ redox systems (referred to ferrocene/ferrocene$^+$ internal reference redox couple FC/FC^+) are collected in Table 1. The observed shifts of the E_{ox} and E_{red} potentials to more positive/negative values can be explained by the electron donating or withdrawing character of the substituent bound to the benzothiazole moiety. E_{red} values of −1.73, −1.96 and −2.03 vs. FC/FC^+ have been found for the organic co-reactants DCN, ABN and DCB, respectively.

Cyclic voltammetry measurements allowed also determining the mean lifetime of the electrode reaction products involved in a particular ECL system. The potential curves show a peak current on the reverse sweeps

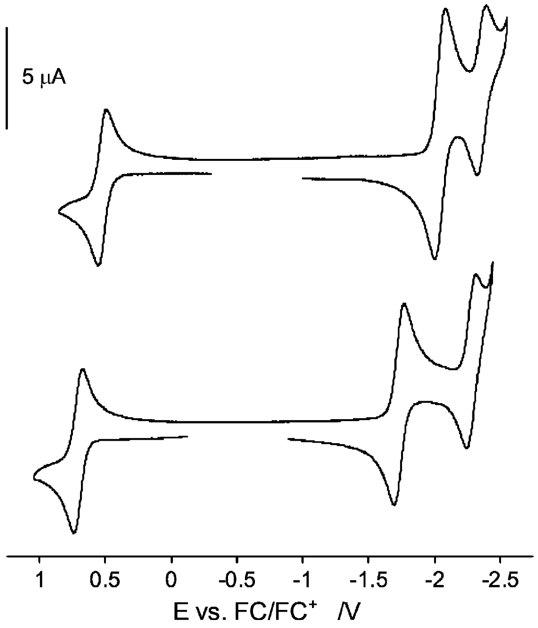

Fig. 2. Cyclic voltammograms recorded (at Pt electrode with scan rate $V_p = 100$ mVs^{-1}) for 1 mM of $(CH_3\text{-pbt})_2Ir(acac)$ and 1 mM of DCB (*top*) or 1 mM of $(CF_3\text{-pbt})_2Ir(acac)$ + 1 mM DCN (*bottom*) in ACN-DX 1:1 solutions containing 0.1 M $TBAPF_6$ as supporting electrolyte.

i_{rp} approximately equal to that of the forward sweep i_{fp}, indicating that the electrode reactions products are quite stable. Only in the case of $(CH_3O\text{-pbt})_2Ir(acac)$ oxidation some deviation from $i_{fp}/i_{rp} = 1$ have been observed. However, based on the anodic to cathodic peak current ratio (recorded at different potential scan rates) it has been found that $L_2Ir(acac)^+$, $L_2Ir(acac)^-$ as well as A^- species are stable within the time scale of the ECL experiments (usually 100 ms).

The application of a triple potential sequence causes a bright, yellow to orange emission (cf. CIE diagram in Fig. 4) to appear in both, the single $L_2Ir(acac)^+/L_2Ir(acac)^-$ and the mixed $L_2Ir(acac)^+/A^-$ ECL systems. The ECL emission bands (see Fig. 3) agree (within an experimental errors) with those observed with photoexcitation. Within experimental error the band-shapes and intensities were found to be independent of the reactant generation sequence. The recorded spectra (see Fig. 3) exhibit traces of the vibronic structures allowing approximate estimation of the excited $^{3*}L_2Ir(acac)$ energies assuming that the emission maxima $\tilde{\nu}_{em}$ correspond to the 0–0 transitions.

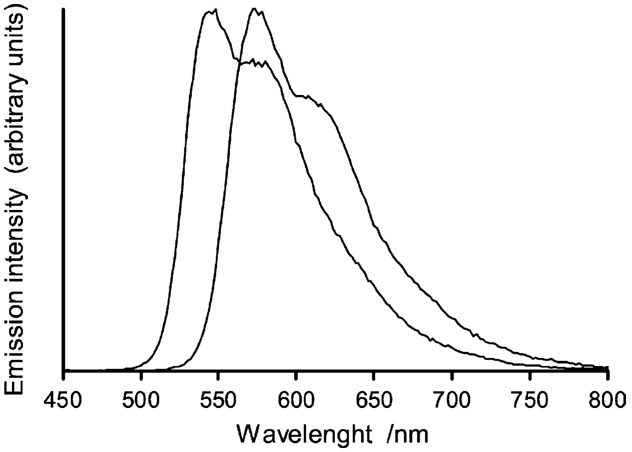

Fig. 3. ECL spectra recorded for 1 mM of $(F\text{-pbt})_2Ir(acac)$ + DCN (*left*) or 1 mM of $(CF_3\text{-pbt})_2Ir(acac)$ + DCN (*right*) in ACN-DX 1:1 solutions containing 0.1 M $TBAPF_6$ as supporting electrolyte.

With the measured E_{ox} and E_{red} values free energy released during ions' annihilation ΔG_{gs} can be straightforwardly calculated according to:

$$\Delta G_{gs} = F(E_{red} - E_{ox}). \quad (5)$$

The ΔG_{gs} term corresponds directly to the exergonicity of the ground state products formation. Correspondingly the exergonicity of the excited $^{3*}L_2Ir(acac)$ states population ΔG_{es} is given by:

$$\Delta G_{es} \approx F(E_{red} - E_{ox}) + hc\tilde{\nu}_{em}. \quad (6)$$

In all cases studied the ΔG_{es} values were negative enough (<−0.15 eV) to enable direct population of the excited species.

Table 1
Summary of spectroscopic, electrochemical and electrochemiluminescence data for $L_2Ir(acac)$ complexes studied

Complex	$\tilde{\nu}_{em}$ (cm^{-1})	ϕ_{em}	E_{ox} (V)	E_{red} (V)	Organic co-reactant	ΔG_{gs} (eV)	ΔG_{es} (eV)	ϕ_{ecl}	ϕ_{es}
$((F\text{-pbt})_2Ir(acac)$	18,350	0.54	+0.70	−2.28	DCN	−2.43	−0.16	0.30	0.56
					ABN	−2.66	−0.39	0.37	0.69
$(CH_3O\text{-pbt})_2Ir(acac)$	18,250	0.46	+0.51	−2.40	DCB	−2.54	−0.28	0.38	0.83
$(CH_3\text{-pbt})_2Ir(acac)$	17,850	0.41	+0.53	−2.35	DCB	−2.56	−0.35	0.22	0.54
$(F_2\text{-pbt})_2Ir(acac)$	17,790	0.46	+0.72	−2.16	DCN	−2.45	−0.24	0.35	0.7
$(pbt)_2Ir(acac)$	17,670	0.44	+0.57	−2.30	DCN	−2.30	−0.11	0.27	0.61
					DCB	−2.60	−0.41	0.32	0.71
$(CF_3\text{-pbt})_2Ir(acac)$	17,360	0.32	+0.79	−2.28	DCN	−2.52	−0.37	0.29	0.91

Luminescence maxima $\tilde{\nu}_{em}$ and luminescence quantum efficiencies ϕ_{em}, redox potentials E_{ox} and E_{red} for one-electron oxidation and reduction of $L_2Ir(acac)$, standard free energies of the ground ΔG_{gs} and the excited state ΔG_{es} population, electrochemiluminescence efficiencies ϕ_{ecl} and efficiencies of the excited $^{3*}L_2Ir(acac)$ population ϕ_{es}.

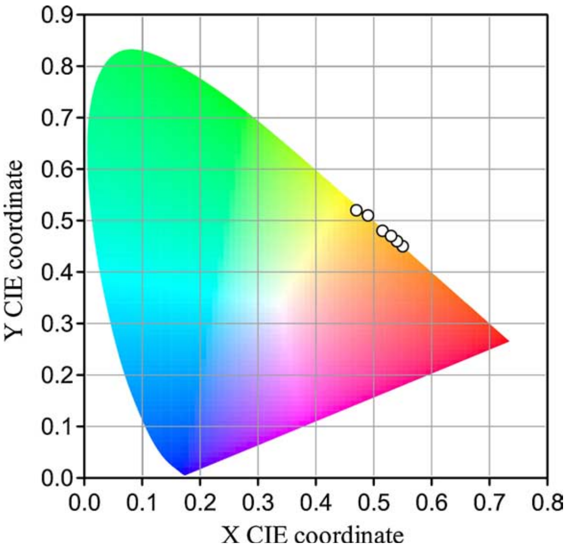

Fig. 4. CIE (*Commission Internationale de l'Éclairage*) coordinates of ECL emission of L_2Ir(acac) complexes. The sequence of the L_2Ir(acac) points corresponds (*clockwise*) to that from Table 1.

Profiles of the ECL transients (at least in the annihilation of L_2Ir(acac)$^+$ and A^- ions) also point to the direct formation of the emitting $^{3*}L_2$Ir(acac). 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. In the cases of the mixed L_2Ir(acac)$^+$/A^- ECL systems $I(\Delta t_R)$ the transient can be linearized according to so-called Feldberg plot

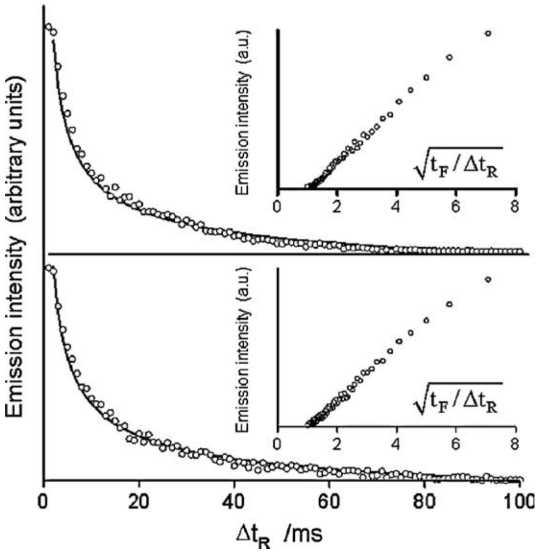

Fig. 5. ECL decay curves recorded for 1 mM (F-pbt)$_2$Ir(acac) + DCN mixed ECL system in ACN-DX 1:1 solutions containing 0.1 M TBAPF$_6$ as supporting electrolyte. Data are presented for two order of the reactants generation: (F-pbt)2Ir(acac)$^+$ – first (*top*) or A^- – first (*bottom*). Solid lines correspond to the fit according to Eq. (7).

$$I(\Delta t_R) = a\sqrt{t_F/\Delta t_R}, \tag{7}$$

where t_F is the time duration of the first, forward potential step. Experimental values of slope-to-intercept ratios $a/b = 0.90 - 1.05$ have been found to be close to the theoretical value of 0.959 (see Fig. 5).

Contrary to the mixed ECL systems studied, intrinsic deviations from linearity in the Feldeberg plots have been found for the single ECL systems investigated. During, the second, reverse step ECL emission intensities drop distinctly faster than expected, suggesting the presence of additional parasitic processes, similarly as it was previously found for Ir(ppy)$_3^+$/Ir(ppy)$_3^-$ system [15]. No attempts were made to determine the nature of the interfering processes, but it is very probable that the observed behavior may be general for the cyclometalated iridium(III) complexes. The parasitic processes mentioned above lead to distinctly lower ECL efficiencies for the single systems, up to one order of magnitude lower as compared to the mixed ones.

In the case of the mixed ECL studied, however, the ECL transients indicate lack or only marginal presence of any additional processes interfering with the excited $^{3*}L_2$Ir(acac) formation. Consequently the measured ECL efficiencies ϕ_{ecl} can be used for estimation of the excited state formation yields ϕ_{es}. In the studied cases, ϕ_{ecl} are related directly to ϕ_{es} by the equation

$$\phi_{ecl} = \phi_{es} \times \phi_0, \tag{8}$$

where ϕ_0 is the emission quantum yield, pertinent property of a given emitter. The determined ϕ_{es} values (cf. Table 1) are brightly large indicating that the excited $^{3*}L_2$Ir(acac) species can be generated nearly quantitatively if appropriate condition of an ECL experiment is chosen, similarly as it was previously reported for the Ir(ppy)$_3^+$/A^- systems [15]. Most probably electrochemical excitation of IrL$_3$ and L_2Ir(acac) complexes occurs according to the same mechanism.

4. Conclusions

The presented results clearly demonstrate that the iridium(III) cyclometalated complexes are especially useful to design new extremely efficient ECL systems. Our preliminary results from the comparative ECL studies involving the analogous complexes with 2-phenylbenzimidazole (pbi) or 2-phenylbenzoxazole (pbo) derivatives additionally support the above conclusion. It can be emphasized that Ir(III) complexes with pbt, pbo or pbi based ligands (relatively easy to synthesize) may offer an interesting alternative to 2-phenylpyridine derivatives investigated till now. We believe also that iridium(III) chelates may be useful in any practical applications (e.g., ECL based analytical methods), similarly to much more elaborated ruthenium(II) complexes.

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