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Electrochemically generated chemiluminescence of tris(2,2′-bipyridine)ruthenium(II), tris(1,10-phenathroline)ruthenium(II) and tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) complexes

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The electrochemically generated chemiluminescence (ECL) of the title complexes with four series of electroactive organic compounds Q in 0.1 M $(C_2H_5)_4NPF_6$ acetonitrile solutions has been studied using a triple-potential-step technique. The yields of the formation of the excited $*RuL_3^{2+}$ ion produced by the electron transfer reaction of RuL_3^+ with aromatic amine or 2,3,7,8-tetramehoxythianthrene radical cations and by the reaction of RuL_3^{3+} with quinone or nitroaromatic radical anions as well as with *N*-methylpyridinium radicals have been determined. A reaction scheme describing generation of the excited $*RuL_3^{2+}$ has been comparatively discussed with that for the quenching reactions with conclusion that spin conversion between two spin forms $^3[RuL_3^{3+/+} \cdots Q^{-/+}]$ and $^1[RuL_3^{3+/+} \cdots Q^{-/+}]$ of an activated complex play a crucial role in both electron transfer processes.

Introduction

Electrochemiluminescence (ECL) from ruthenium(II) chelates RuL_3^{2+} occurs in electron transfer (ET) processes according to the mechanism commonly accepted in the literature.[1–11] In the electrochemical reactions the parent ion RuL_3^{2+} undergoes one-electron reduction and oxidation to RuL_3^+ and RuL_3^{3+} species:

$$RuL_3^{2+} + e^- \leftrightarrows RuL_3^+ \tag{1a}$$

$$RuL_3^{2+} - e^- \leftrightarrows RuL_3^{3+} \tag{1b}$$

Reduced RuL_3^+ and oxidized RuL_3^{3+} ions annihilate with the formation of the excited $*RuL_3^{2+}$ state and subsequent emission of light:

$$RuL_3^+ + RuL_3^{3+} \longrightarrow RuL_3^{2+} + {*RuL_3^{2+}} \tag{2a}$$

$$RuL_3^+ + RuL_3^{3+} \longrightarrow RuL_3^{2+} + RuL_3^{2+} \tag{2b}$$

Sufficiently low energies of the excited $*RuL_3^{2+}$ states also allow for the experimental observation of ECL phenomena in mixed systems,[12] *i.e.*, in the reactions between RuL_3^+ and strong oxidants or between RuL_3^{3+} and strong reductants. For example, electron transfer (ET) reaction between stable radical cations D^+ (*e.g.*, formed in the one-electron oxidation of aromatic amines D) and RuL_3^+ leads to more or less efficient $*RuL_3^{2+}$ generation:

$$RuL_3^+ + D^+ \longrightarrow {*RuL_3^{2+}} + D \tag{3a}$$

$$RuL_3^+ + D^+ \longrightarrow RuL_3^{2+} + D \tag{3b}$$

In a similar way $*RuL_3^{2+}$ generation may take place during ET reaction between RuL_3^{3+} and stable radical anions A^- (*e.g.*, formed in the one-electron reduction of aromatic nitrocompounds or quinones A):

$$RuL_3^{3+} + A^- \longrightarrow {*RuL_3^{2+}} + A \tag{4a}$$

$$RuL_3^{3+} + A^- \longrightarrow RuL_3^{2+} + A \tag{4b}$$

Correspondingly, neutral organic radicals $R^•$ (*e.g.*, formed in the one-electron reduction of *N*-methylpyridinium cations R^+) may also be applied as reducing agent, with a reaction scheme similar to (4a), (4b), but with $R^•$ and R^+ redox forms involved instead of A^- and A, respectively. Excited state generation of the organic co-reactants is not included in the above reaction's pattern because their energies are usually high enough and their population is an energetically unfavourable process.

According to the discussed reaction patterns, the ECL efficiency (in photons emitted per electrons transferred between reduced and oxidized forms of the parent molecules) is related directly to the yield of the excited state generation (ϕ_{es}) and to the emission quantum yield (ϕ_o) of a given emitter $*RuL_3^{2+}$ ($\phi_{ecl} = \phi_{es} \times \phi_o$). More detailed and quantitative discussion of the ϕ_{ecl} value for the given ECL system may be done in terms of an ET model for chemiluminescence,[13] first proposed by Marcus. Electron transfer between oxidized and reduced reactants leads competitively to the population of the excited state (low exergonic reactions (2a)–(4a)) or to the ground state (high exergonic reactions (2b)–(4b)).

It should be noted, however that the above approach is somewhat oversimplified from the mechanistic point of view (*cf.* Fig. 1). The electrochemically generated, oxidized and reduced species form (in the diffusion controlled process) an

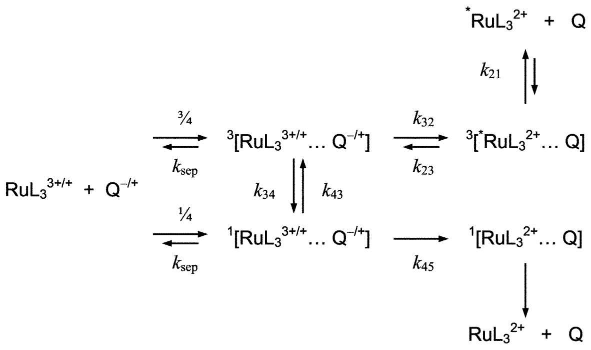

Fig. 1 Reaction mechanism for excited $*RuL_3^{2+}$ generation in the oxidative ($RuL_3^+ + Q^+$) and reductive ($RuL_3^{3+} + Q^-$) ions annihilation processes.

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activated complex (presumably a contact ion pair) in two different spin states with (according to the spin statistic rule)[14,15] a branching ratio of 3 : 1. It is expected that the generation of $^*RuL_3^{2+}$ from the triplet $^3[RuL_3^{3+/+} \cdots Q^{-/+}]$ precursor is much more efficient with respect to the singlet $^1[RuL_3^{3+/+} \cdots Q^{-/+}]$ one. Electron transfer (with rate k_{32}) within the activated complex in the triplet state $^3[RuL_3^{3+/+} \cdots Q^{-/+}]$ leads directly to the generation of excited $^*RuL_3^{2+}$. On the other hand, triplet–singlet conversion (with the rate k_{34}) is necessary before electron transfer to the ground state product occurs. An activated complex $^1[RuL_3^{3+/+} \cdots Q^{-/+}]$ in the singlet state exhibits exactly opposite behaviour. Electron transfer leads directly to the ground state products (with rate k_{45}) but the excited $^*RuL_3^{2+}$ formation is preceded by singlet–triplet conversion (with rate k_{43}). Taking into account presumably very small energy splitting between two spin forms of the activated complex one can conclude that $3k_{43} \approx k_{34}$.

The kinetic scheme for the electron transfer generation of excited $^*RuL_3^{2+}$ can be simply solved (similarly to the case of the quenching processes)[16] using the steady-state approximation:

$$\frac{\phi_{es}}{1-\phi_{es}} = \frac{3k_{21}k_{32}/(k_{23}+k_{21})}{k_{45}} \times \frac{k_{sep}+4k_{34}+k_{45}}{k_{sep}+4k_{34}+k_{21}k_{32}/(k_{23}+k_{21})} \qquad (5)$$

where the $k_{21}k_{32}/(k_{23} + k_{21})$ term (an effective rate of the excited state population) also takes into account diffusion controlled separation of the ET product $[^*RuL_3^{2+} \cdots Q]$ into bulk solution.

ET quenching of the excited $^*RuL_3^{2+}$ should be essentially the reverse process to that proposed for the ECL reactions and may be quantitatively discussed according to the reaction scheme[17–19] presented in Fig. 2 where k_{12} and k_{21} are the diffusion controlled forward and reverse rate constants for the formation of an activated complex between excited $^*RuL_3^{2+}$ and quencher Q. The activated complex is formed from the excited triplet state of RuL_3^{2+} so that (because of the spin conservation rule) the ET product also appears (with the forward electron transfer rate k_{23}) in the triplet state. As usual, the redox products $Q^{-/+}$ and $RuL_3^{3+/+}$ may be separated in solutions, with the rate k_{sep} and the efficiency $\phi_{sep} \approx k_{sep}/(k_{sep} + k_{34})$, if the recombination to the singlet ground state product is sufficiently slow. The latter is allowed from the singlet precursor, but forbidden from the triplet one. Therefore, the triplet–singlet conversion, occurring with the rate k_{34}, is a necessary step that makes back electron transfer to the ground state product (with rate k_{45}) possible. The scheme also includes reverse electron transfer corresponding to back electron transfer to the excited state (with rate k_{32}) and singlet–triplet conversion (with rate k_{43}). The latter process is relatively slow[17,18] ($k_{43} \ll k_{45}$) as compared to the ground product formation and may be, at least in a first-order approximation, neglected. On the other hand, the back electron transfer to the ground state products is relatively fast[17,18] ($k_{45} \gg k_{sep}$) which allows us to neglect the separation of $^1[RuL_3^{3+/+} \cdots Q^{-/+}]$ into isolated products $RuL_3^{3+/+}$ and $Q^{-/+}$.

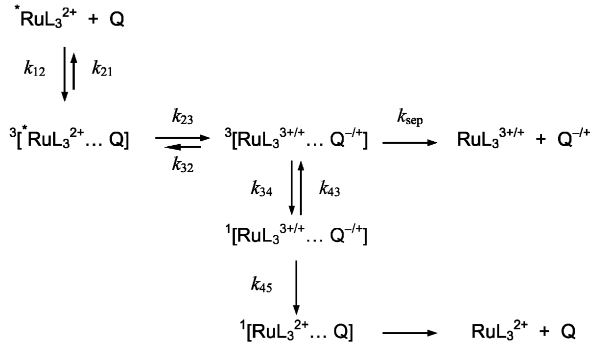

Fig. 2 Reaction mechanism for the electron transfer quenching of excited $^*RuL_3^{2+}$.

The observed bimolecular quenching rate constant k_q is related to the rate constants of all the reaction steps. The kinetic scheme as discussed above may be easily solved in the steady-state approximation.[16] Assuming the above-mentioned simplifications, *i.e.*, $k_{43} \ll k_{45}$ and $k_{45} \gg k_{sep}$ the quenching rate constant k_q may be expressed as follows:

$$k_q = k_{12} / \left(1 + \frac{k_{21}}{k_{23}} + \frac{k_{32}}{k_{23}} \frac{k_{21}}{(k_{34} + k_{sep})}\right) \qquad (6)$$

For a given quencher Q all the rate constants in the ET quenching scheme can be determined by means of the fluorescence quenching and transient absorption data. Taking into account the intuitive relationship between two classes of the ET processes one can expect that the same set of kinetic parameters can be applied to the quantitative description of ECL efficiencies.

More detailed investigations of the above-mentioned relationship have been recently performed in our laboratory for the mixed ECL systems involving tris(2,2′-bipyridine)ruthenium(II) $Ru(bipy)_3^{2+}$ complex.[12] As was expected (and reported previously for other ECL systems, *e.g.*, ref. 20) the functional dependence on the ions annihilation exergonicity (ΔG_{es}) was found for both $Ru(bipy)_3^{+}$–oxidant and $Ru(bipy)_3^{3+}$–reductant systems. It has been found that the experimentally determined ϕ_{ecl} value increases and approaches a limiting value as ΔG_{es} increases. Somewhat surprisingly, however, the observed relationship between ϕ_{ecl} and ΔG_{es} has been found to be nonuniform. For the same ΔG_{es} the ECL efficiency depends on the nature of the organic reaction partners with the experimental points having a tendency to cluster (*cf.* Fig. 3) around two different curves corresponding to relatively efficient (hec type) or inefficient (lec type) ECL systems. Moreover the kinetic parameters derived from the quenching data have allowed us to make a successful quantitative description of the ECL efficiencies for $Ru(bipy)_3^{2+}$ ECL systems of the hec type.[12,21] In contrast, for the ECL systems assigned to the lec type a similar approach using the experimental quenching data[22] leads to discrepancies as large as a few orders of magnitude.

According to the postulated reaction mechanisms the triplet–singlet conversion within $^3[RuL_3^{3+/+} \cdots Q^{-/+}]$ and $^1[RuL_3^{3+/+} \cdots Q^{-/+}]$ forms of an activated complex play a crucial role in both discussed ET processes. The smaller k_{34} is the larger the ECL and product separation efficiencies in ET quenching processes are expected to be. Principally the k_{34} rate should depend on the nature of the quenched complex ion as well as on the quencher used. Results from extensive studies performed for the oxidative and reductive ET quenching of the $Ru(bipy)_3^{2+}$ ion[17,18,21,23–30] indicate that the triplet–singlet conversion rate k_{34} is relatively weakly dependent on the nature of the organic co-reactant. On the other hand, replacing 2,2′-bipyridine by an another ligand (*e.g.*, 4,7-diphenyl-1,10-phenanthroline) leads to much more pronounced changes in the k_{34} values.[25] The measured separation efficiencies ϕ_{sep} of the ET reaction (for a given quencher Q) are distinctly smaller indicating the intrinsic increase of the k_{34} rate by approximately one order of magnitude. It may be expected that a similar behaviour (changes in the ϕ_{es} efficiencies) should also be observed in ECL experiments. Experimental verification of the above hypothesis may lead to a better understanding of the triplet–singlet conversion role in the quantitative description of ECL phenomena and to an eventual explanation of the observed differences between ECL systems of the hec and lec type which was the main purpose of the presented work.

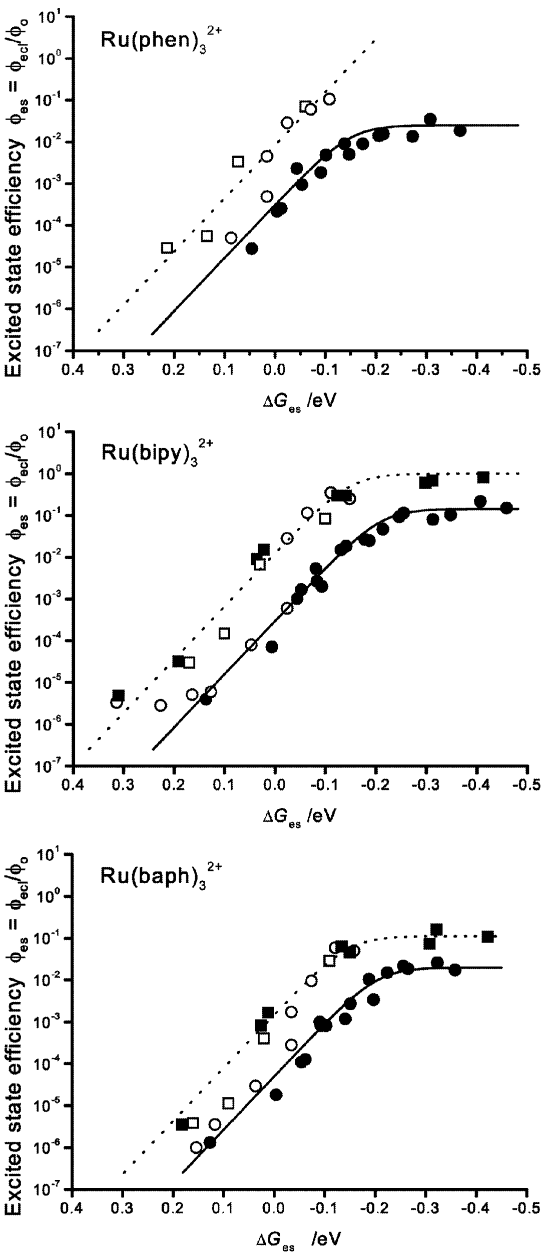

Fig. 3 Plot of ϕ_{es} *versus* ΔG_{es} for the ECL systems involving Ru(phen)$_3^{2+}$ (top), Ru(bipy)$_3^{2+}$ (middle) and Ru(baph)$_3^{2+}$ (bottom) ions in 0.1 M $(C_2H_5)_4NPF_6$ acetonitrile solutions. Data for the ECL systems with nitrocompounds (●), quinones (○), *N*-methylpyridinium cations (□) and aromatic amines or 2,3,7,8-tetramethoxythianthrene (■).

Experimental

Chemicals

Tris(2,2′-bipyridine)ruthenium(II), Ru(bipy)$_3^{2+}$, tris(1,10-phenanthroline)ruthenium(II), Ru(phen)$_3^{2+}$, and tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II), Ru(baph)$_3^{2+}$, (as perchlorate salts) were synthesized using procedures described in the literature[31,32] and purified by means of re-crystallization from acetonitrile/toluene mixtures. The pyridinium salts were synthesised by addition of methyl iodide to an acetone solution of the appropriately substituted pyridine. Pyridinium hexafluorophosphate salts were obtained by the addition of KPF_6 to an aqueous solution of the iodo salt followed by re-crystallisation from water. Commercially available amines, quinones or nitroaromatics were purified by the conventional manner (crystallisation or sublimation for solids and fractional distillation for liquids). 2,3,7,8-Tetramethoxythianthrene[33] and 2,3,5,6-tetramethoxy-1,4-benzoquinone[34] were synthesised as described in the literature. 3-Nitrofluoranthene and 8-nitrofluoranthene were synthesised by nitration of fluoranthene in acetic acid solutions,[35] followed by fractional crystallisation from nitroethane. Tetraethylammonium hexafluorophosphate was prepared by metathesis of $(C_2H_5)_4NBr$ with KPF_6 in aqueous solutions. The precipitated product was washed with water and re-crystallised from anhydrous methanol. Before use, the supporting electrolytes were dried in a vacuum (at 100 °C) for 12 h. Acetonitrile (ACN) and butyronitrile (BN) were dried and purified for electrochemical and spectroscopic use in a conventional manner. The solutions studied were deaerated with pure argon, which was presaturated by bubbling through the solvent used.

Measurements

A home-built measurement setup (described previously in refs. 21, 36 and 37) was used for both electrochemical and ECL studies. Cyclic voltammetry was run prior to the ECL experiments to evaluate the electrochemical characteristics and to check the temporal stability of the electrochemical reaction products. The cyclic voltammetry experiments also allowed us to determine the redox potentials E_{ox} and E_{red} of the given reactants (within an experimental error of ±10mV), as well as the mean lifetime of the reactants involved in a particular ECL process. The obtained E_{ox} and E_{red} values were in good agreement with the data reported in the literature. It was also found that the reactants' lifetimes are longer than the time of the ECL experiment (usually 100 ms). Thus, it may be expected that during the ECL experiment time, only the ion annihilation reaction takes place.

ECL due to the electron transfer reaction between the reduced and oxidized forms of the reactants in 0.1 M $(C_2H_5)_4NPF_6$ ACN was studied using the triple-potential-step technique.[38–41] The potential limits of the programmed sequence were chosen so as to ensure subsequent electrochemical generation of the active intermediates in the mass-transfer-controlled region. ECL yields were determined against the standard, *i.e.*, Ru(bipy)$_3^{3+}$ + Ru(bipy)$_3^{+}$ ECL system in ACN solution containing 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ (with $\phi_{ecl} = 0.05$ from ref. 6), taking also into account the differences in the charges passed through the studied solution. In a given solution, two or three records were made to check the temporal stability of the system studied. The values of the integrated photon intensities were obtained as averages of several independent measurements. The error limit of the above procedure was estimated to be *ca.* 10–15%. The sensitivity threshold of the detection part of our equipment was about 10^{-7}.

Absorption spectra were run on a Shimadzu UV 2401 spectrophotometer. Steady-state luminescence spectra were recorded using an Edinburgh FS 900 CDT fluorometer with quinine sulfate in 0.1 N H_2SO_4 ($\phi_o = 0.51$) as a standard for the quantum yield determinations. Luminescence lifetimes were measured using an Edinburgh FL 900 CDT time-resolved fluorometer. Samples for quenching measurements in 0.1 M $(C_2H_5)_4NPF_6$ ACN solutions contained 1–3 × 10^{-5} M of Ru(baph)$_3^{2+}$ complex with the appropriate concentration of added quencher. Emission measurements have been performed for solutions containing a few different concentrations of the quencher C_Q, using Ru(baph)$_3^{2+}$ solutions without added quencher as a standard for the emission intensity determination. The quenching rate constants k_q were determined by the steady-state Stern–Volmer method[16] with the estimated error in the determination of k_q values found to be smaller than 10–15%.

Results and discussion

Application of a triple-step potential sequence (within the limits of 1e reduction and 1e oxidation of the given reactants)

Table 1 Summary of the electrochemical and spectroscopic data for the RuL_3^{2+} complexes studied. Redox potentials (E_{ox} and E_{red}), luminescence maxima ($\tilde{\nu}_{lum}$), quantum efficiencies (ϕ_o) and lifetimes (τ_{lum}) in acetonitrile solutions at room temperature and 77 K luminescence 0–0 transitions ($\tilde{\nu}_{0-0}$) in butyronitrile glass

Complex	E_{ox}/V	E_{red}/V	$\tilde{\nu}_{lum}$/cm^{-1}	ϕ_o	τ_{lum}/μs	$\tilde{\nu}_{0-0}$/cm^{-1}
$Ru(bipy)_3^{2+}$	+0.88	−1.73	16340	0.06	0.85	17250
$Ru(phen)_3^{2+}$	+0.89		16670	0.02	0.40	17620
$Ru(baph)_3^{2+}$	+0.84	−1.69	16130	0.22	5.50	16860

[a] Redox potentials according to ferrorocene/ferricinium internal reference redox couple (with E_{ox} = +0.41 V *vs.* aqueous saturated calomel electrode). Electrochemical reduction of $Ru(phen)_3^{2+}$ in ACN solutions is strongly perturbed by surface phenomena (probably absorption of $Ru(phen)_3^{+}$, *cf.* ref. 4) and does not correspond to a simple one-electron reduction. [b] Luminescence data (ϕ_o and τ_{lum} values) for $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ from refs. 44 and 45, respectively. Data for $Ru(baph)_3^{2+}$ from the measurements performed within this work.

causes emission from the excited $^*RuL_3^{2+}$ ions with the ECL spectra the same as those observed upon photoexcitation. As expected, the functional dependence of ϕ_{ecl} on the electron transfer reaction exergonicity is observed for all RuL_3^{2+}–donor and RuL_3^{2+}–acceptor systems studied (*cf.* Table 2). ϕ_{ecl} rapidly increases and approaches a limiting value with the increase of ΔG_{es} given by the difference between the oxidation (E_{ox}) and the reduction potential (E_{red}) of the involved reactants and the energy E_{MLCT} of the excited $^*RuL_3^{2+}$:

$$\Delta G_{es} = F(E_{red} - E_{ox}) + E_{MLCT} \tag{7}$$

where F is the Faraday constant. ΔG_{es} have been calculated according to eqn. (7) using E_{MLCT} = 2.10 eV[42,43] for $^*Ru(bipy)_3^{2+}$. Corresponding E_{MLCT} values of 2.15 eV for $^*Ru(phen)_3^{2+}$ and 2.05 eV for $^*Ru(baph)_3^{2+}$ have been estimated by comparison of their 77 K and room temperature luminescence spectra with that for $Ru(bipy)_3^{2+}$ taking into account shifts in the maxima positions (*cf.* Table 1).

For all three complexes studied the observed relationship between ϕ_{ecl} and ΔG_{es} (*cf.* Table 2 and Fig. 3) is non-uniform and for the same ΔG_{es} value (also after correction for the rather small Coulombic repulsion/attraction between ET reactants/products as calculated according to the familiar Debye equation)[46,47] the ECL efficiency depends on the nature of the organic reaction partner. The experimental points have a tendency to cluster around two different curves. The behaviour of both $Ru(baph)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes is very similar to that found previously for $Ru(bipy)_3^{2+}$ with similar differences between ECL efficiencies for systems of the hec and lec types. The most important finding arises from the comparison of the excited state efficiencies ϕ_{es} calculated using the quantum yield ϕ_o of the given emitter $^*RuL_3^{2+}$. For the given reaction exergonicity ΔG_{es}, the experimentally found ϕ_{es} value depends on the ligand nature in the RuL_3^{2+} complex (*cf.* Fig. 3). In the case of $Ru(baph)_3^{2+}$ the efficiencies ϕ_{es} are distinctly smaller as compared to the $Ru(bipy)_3^{2+}$ ion. The effect is less pronounced for $Ru(phen)_3^{2+}$ but still observed, especially if the efficiencies ϕ_{es} are compared taking into account small energetic differences between RuL_3^{2+}–Q systems for a given organic co-reactant. It was done using a semi-statistical approach based on an empirical relation (exponential growth function $[\alpha + \beta\exp(\gamma\Delta G_{es})]^{-1}$) between ϕ_{es} and ΔG_{es} values. Fitting procedures have been performed for all six groups of the studied ECL systems assuming the same γ but varying α and β parameters. The obtained results indicate that the ECL systems involving $Ru(phen)_3^{2+}$ or $Ru(baph)_3^{2+}$ complexes are statistically less efficient as compared to $Ru(bipy)_3^{2+}$ by factors 1.5–2 and 6–8, respectively. For a given RuL_3^{2+} complex, however, quantitative differences in ϕ_{es} efficiencies between ECL systems of the hec and lec type remain more or less the same.

The observed differences between efficiencies ϕ_{es} of the ECL systems studied may be probably attributed to the ligand-introduced changes in the rates of the excited state and/or the ground state formation. Quantitative discussion of the above options would be possible in view of appropriate quenching data but unfortunately this is mostly only available for the $Ru(bipy)_3^{2+}$ complex. However, our preliminary results from the quenching studies performed for $Ru(phen)_3^{2+}$ and $Ru(baph)_3^{2+}$ ions suggest that the k_q rates depend on the quenching exergonicity ΔG_q ($\Delta G_q = -\Delta G_{es}$) in the usual way. At the same ΔG_q k_q values are only weakly sensitive to the complex type. Because the measured quenching rate constants k_q are more sensitive to k_{23} or k_{32} than to k_{34} one can conclude that the ligand introduced changes in the triplet–singlet conversion within an activated complex $[RuL_3^{3+/+} \cdots Q^{-/+}]$ are mostly responsible for the observed ECL behaviour. A more detailed analysis for the RuL_3^{2+}–R^+ systems (described below) support the above conclusion.

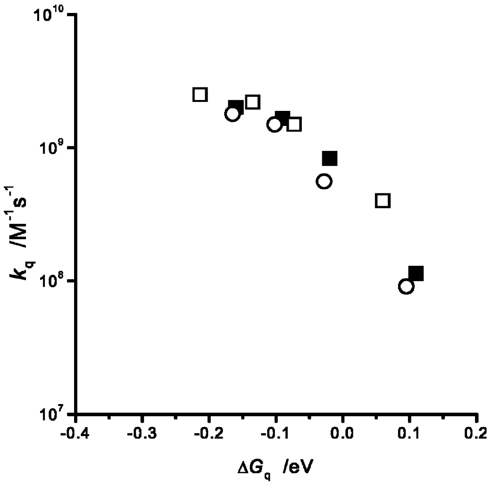

Fig. 4 Electron transfer quenching rate constant k_q of the excited $^*RuL_3^{2+}$ in 0.1 M $(C_2H_5)_4NPF_6$ acetonitrile solutions as a function of the reaction exergonicity ΔG_q in the oxidative quenching reactions $^*RuL_3^{2+}$ + R^+. Data for $Ru(bipy)_3^{2+}$ (○), $Ru(phen)_3^{2+}$ (□) and $Ru(baph)_3^{2+}$ (■) complexes.

The rate constants k_q for the quenching of $^*RuL_3^{2+}$ complexes (in ACN solutions containing 0.1 M $(C_2H_5)_4PF_6$) are summarised in Table 3 together with the estimated ΔG_q values. As expected, the more exergonic the electron transfer process, the faster quenching is observed. The observed relationship between k_q and ΔG_q (shown in Fig. 4) is, as already stated above, quite uniform. Relatively small values of k_q are below the diffusional limitation for bimolecular reactions and, consequently, correspond directly to an activation-controlled process. If the diffusional limitation can be neglected (as it is in the present case), the expression for the overall quenching rate, eqn. (6), may be simplified to:

$$k_q = \frac{k_{12}k_{23}(k_{34} + k_{sep})}{k_{21}(k_{32} + k_{34} + k_{sep})} = \frac{K_{12}k_{23}(k_{34} + k_{sep})}{(k_{32} + k_{34} + k_{sep})} \tag{8}$$

On the other hand results from transient absorption[21] as well as from ECL studies indicate that the sum k_{34} + k_{sep} is much larger, at least by one order of magnitude, than k_{32}. Thus,

Table 2 Redox potentials of the organic co-reactant (E_{ox} and E_{red}), and ECL efficiencies (ϕ_{ecl}) for the ECL systems studied

ECL system type/complex	E_{ox}/V	E_{red}/V	ϕ_{ecl}		
			$Ru(bipy)_3^{2+}$	$Ru(phen)_3^{2+}$	$Ru(baph)_3^{2+}$
$Ru(bipy)_3^+ + D^+$ where D =					
N,*N*,*N′*,*N′*-Tetramethylbenzidine	+0.06		~2.9 × 10^{-7}		
N,*N*-Dimethyl-*p*-anisidine	+0.18		1.9 × 10^{-6}		7.8 × 10^{-7}
N,*N*-Dimethyl-*p*-toluidine	+0.33		5.4 × 10^{-4}		1.8 × 10^{-4}
N-Methylphenothiazine	+0.35		9.1 × 10^{-4}		3.7 × 10^{-4}
2,3,7,8-Tetramethoxythianthrene	+0.49		1.8 × 10^{-2}		1.4 × 10^{-2}
4-(Dimethylamino)chlorobenzene	+0.51		1.8 × 10^{-2}		1.0 × 10^{-2}
4-(Dimethylamino)acetophenone	+0.67		3.6 × 10^{-2}		1.6 × 10^{-2}
Ethyl 4-(dimethylamino)benzoate	+0.68		4.1 × 10^{-2}		3.5 × 10^{-2}
4-(Dimethylamino)benzonitrile	+0.78		4.9 × 10^{-2}		2.4 × 10^{-2}
$Ru(bipy)_3^{3+} + R^\bullet$ where R^+ = (as PF_6^- salts)					
4-Cyano-*N*-methylpyridinium		−1.05	1.8 × 10^{-6}	5.8 × 10^{-7}	8.4 × 10^{-7}
4-Aceto-*N*-methylpyridinium		−1.12	9.0 × 10^{-6}	1.1 × 10^{-6}	2.5 × 10^{-6}
4-Carboethoxy-*N*-methylpyridinium		−1.19	4.0 × 10^{-4}	6.7 × 10^{-5}	8.9 × 10^{-5}
4-Amido-*N*-methylpyridinium		−1.32	5.0 × 10^{-3}	1.4 × 10^{-3}	6.3 × 10^{-3}
$Ru(bipy)_3^{3+} + A^-$ where A =					
1,4-Benzoquinone		−0.91	~2.0 × 10^{-7}		
Tetramethoxy-1,4-benzoquinone*		−1.06	3.1 × 10^{-7}		~2.2 × 10^{-7}
1,4-Naphthoquinone		−1.09	3.6 × 10^{-7}		7.8 × 10^{-7}
2-Methyl-1,4-naphthoquinone		−1.17	4.8 × 10^{-6}	1.0 × 10^{-6}	6.5 × 10^{-6}
Duroquinone		−1.24	3.6 × 10^{-5}	9.8 × 10^{-6}	6.2 × 10^{-5}
2-Chloro-9,10-anthraquinone		−1.24	1.7 × 10^{-3}	9.0 × 10^{-5}	3.8 × 10^{-4}
1-Chloro-9,10-anthraquinone		−1.28	6.9 × 10^{-3}	5.7 × 10^{-4}	2.1 × 10^{-3}
9,10-Anthraquinone		−1.33	2.1 × 10^{-2}	1.2 × 10^{-3}	1.3 × 10^{-2}
2-Methyl-9,10-anthraquinone		−1.37	1.5 × 10^{-2}	2.1 × 10^{-3}	1.1 × 10^{-2}
p-Dinitrobenzene		−1.08	~2.4 × 10^{-7}		~2.9 × 10^{-7}
o-Dinitrobenzene		−1.21	4.3 × 10^{-6}	5.6 × 10^{-7}	4.0 × 10^{-6}
p-Cyanonitrobenzene		−1.26	6.1 × 10^{-5}	4.3 × 10^{-7}	2.4 × 10^{-5}
p-Nitrobenzaldehyde		−1.27	1.0 × 10^{-4}	5.1 × 10^{-6}	2.8 × 10^{-5}
3-Nitrofluoranthene		−1.30	3.2 × 10^{-4}		2.2 × 10^{-4}
8-Nitrofluoranthene		−1.30	1.6 × 10^{-4}	4.6 × 10^{-5}	1.8 × 10^{-4}
m-Dinitrobenzene		−1.31	1.2 × 10^{-4}	1.9 × 10^{-5}	1.8 × 10^{-4}
Methyl 4-nitrobenzoate		−1.35	9.0 × 10^{-4}	3.7 × 10^{-5}	2.6 × 10^{-4}
p-Trifluoromethylnitrobenzene*		−1.36	1.1 × 10^{-3}	9.7 × 10^{-5}	6.0 × 10^{-4}
o-Trifluoromethylnitrobenzene*		−1.40	1.6 × 10^{-3}	1.8 × 10^{-4}	2.3 × 10^{-3}
p-Nitrobenzamide*		−1.41	1.5 × 10^{-3}	1.0 × 10^{-4}	7.5 × 10^{-4}
m-Nitrobenzaldehyde		−1.43	2.8 × 10^{-3}	1.8 × 10^{-4}	3.3 × 10^{-3}
Methyl 3-nitrobenzoate		−1.47	5.5 × 10^{-3}	2.8 × 10^{-4}	4.8 × 10^{-3}
p-Chloronitrobenzene		−1.48	6.9 × 10^{-3}	3.1 × 10^{-4}	4.1 × 10^{-3}
p-Fluoronitrobenzene		−1.53	4.8 × 10^{-3}	2.7 × 10^{-4}	5.7 × 10^{-3}
Nitrobenzene		−1.57	6.2 × 10^{-3}	6.9 × 10^{-4}	3.8 × 10^{-3}
p-Nitrotoluene		−1.63	1.3 × 10^{-2}	3.7 × 10^{-4}	
p-Nitroanisole		−1.68	9.0 × 10^{-3}		

[a] Redox potentials according to ferrorocene/ferricinium internal reference redox couple (with E_{ox} ~ +0.41 *vs.* aqueous saturated calomel electrode). [b] ECL systems of RuL_3^{2+}–D type have been not studied for $Ru(phen)_3^{2+}$ because of the poor reproducibility of the ECL results. [c] Data for ECL systems involving $Ru(bipy)_3^{2+}$ are taken mostly from ref. 12 (data measured in this work are marked with a *); data for $Ru(phen)_3^{2+}$–R^+ECL system from ref. 21.

k_{23} and k_{32} rate constants can be simply evaluated from the experimental values of k_q:

$$k_{23} = k_q/K_{12} \tag{9a}$$

and

$$k_{23}/k_{32} = \exp[-(\Delta G_{es} + w_R - w_P)/RT] \tag{9b}$$

using the formation constant of the activated complex k_{12} as straightforwardly calculated according to the Fuoss–Eigen model:[48,49]

$$K_{12} = \frac{4\pi N_A\, d^3}{3000}\exp(-w_R/RT) \tag{10}$$

where N_A, R and T are the Avogadro constant, the gas constant and absolute temperature, respectively. Terms w_p and w_R in eqns. (9) and (10) correspond to the Coulomb interaction energies required to bring the reactants (w_R = +0.03–0.04 eV) or products (w_P = 0 eV) together at the most probable separation distance d at which the electron transfer takes place. It should be noted, however, that the knowledge of the exact value of the w_R term is not necessary for k_{32} estimation. In the particular case of RuL_3^{2+}–R^+ systems the contribution of the w_R to K_{12} and ($\Delta G_{es} + w_R - w_P$) terms is cancelled. Taking into account the effective radii[50] of $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ (0.71 nm) and R^+ (0.39 nm) an ion separation distance of d = 1.1 nm has been assumed in k_{32} estimation. In the case of $Ru(baph)_3^{2+}$–R^+ systems $d \approx 1.5$ nm seems to be more appropriate because of a steric hindrance of the phenyl group in 4,7-diphenyl-1,10-phenanthroline ligand. The obtained k_{32} values are presented in Table 3.

The same assumption as made in the case of quenching reactions (*i.e.*, $k_{23} < k_{21}$ and $k_{45} > k_{34}$) allows us to simplify the expression (eqn. (5)) describing efficiencies of the excited state formation in an ECL process. Assuming lack of the diffusional

Table 3 Quenching and ECL data for RuL_3^{2+} + R^+ systems: Gibbs energies for the excited $^*RuL_3^{2+}$ ET quenching (ΔG_q), experimental values of the quenching rate constants (k_q), efficiencies of the excited $^*RuL_3^{2+}$ formation (ϕ_{es}), estimated values of the ECL forward electron transfer reaction (k_{32}) and triplet–singlet conversion rates (k_{34})

Complex	Quencher	ΔG_q/eV	k_q/$M^{-1}s^{-1}$	ϕ_{es}	k_{32}/s^{-1}	k_{34}/s^{-1}	
$Ru(bipy)_3^{2+}$	PAM^+	0.10	9.1×10^7	8.3×10^{-2}	1.4×10^9	1.1×10^{10}	(1.7×10^{10})
	PCE^+	−0.03	5.6×10^8	6.7×10^{-3}	5.3×10^7	5.9×10^9	(1.5×10^{10})
	PAC^+	−0.10	1.5×10^9	1.5×10^{-4}	5.2×10^6	4.6×10^{10}	(1.3×10^{10})
	PCN^+	−0.17	1.8×10^9	3.0×10^{-5}	7.2×10^5	1.8×10^{10}	(5.4×10^9)
$Ru(phen)_3^{2+}$	PAM^+	0.06	4.0×10^8	7.0×10^{-2}	1.3×10^9	1.3×10^{10}	(2.3×10^{10})
	PCE^+	−0.07	1.5×10^9	3.4×10^{-3}	3.0×10^7	6.6×10^9	(2.8×10^{10})
	PAC^+	−0.14	2.3×10^9	5.5×10^{-5}	2.9×10^6	4.0×10^{10}	(2.3×10^{11})
	PCN^+	−0.21	2.5×10^9	2.9×10^{-5}	2.1×10^5	5.4×10^9	(3.0×10^{10})
$Ru(baph)_3^{2+}$	PAM^+	0.11	1.1×10^8	2.9×10^{-2}	1.3×10^9	3.3×10^{10}	
	PCE^+	0.02	8.3×10^8	4.0×10^{-4}	5.8×10^7	1.1×10^{11}	
	PAC^+	−0.09	1.7×10^9	1.1×10^{-5}	7.6×10^6	5.0×10^{11}	
	PCN^+	−0.16	2.0×10^9	3.0×10^{-6}	6.0×10^5	1.5×10^{11}	

[a] PAM^+, PCE^+, PAC^+ and PCN^+ are the abbreviations for the 4-amido-*N*-methylpyridinium, 4-carboethoxy-*N*-methylpyridinium, 4-aceto-*N*-methylpyridinium and 4-cyano-*N*-methylpyridinium cations, respectively. [b] Values of k_q for $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ from ref. 21. Data for $Ru(baph)_3^{2+}$ were determined by a steady-state Stern–Volmer method (measured in this work). [c] Values of k_{32} and k_{34} constants estimated according to eqns. (9) and (11), respectively. k_{34} values in parentheses (data from transient absorption studies taken from ref. 21) are presented for comparison.

limitation and taking into account relatively small values of ϕ_{es} efficiencies one can simply obtain:

$$\frac{\phi_{es}}{1-\phi_{es}} = \frac{3k_{32}}{4k_{34}+k_{32}} \approx \frac{3k_{32}}{4k_{34}} \tag{11}$$

Using the k_{32} values (obtained as described above from the k_q constants) eqn. (11) allows for estimation of the triplet–singlet conversion rate constants k_{34}. The obtained k_{34} values are presented in Table 3 with the corresponding literature data[21] from the transient absorption studies. Nice agreement between both sets of the k_{34} constants for $Ru(bipy)_3^{2+}$–R^+ and $Ru(phen)_3^{2+}$–R^+ systems allows us to conclude that all approximations made in the quenching and ECL data analysis are fulfilled. The obtained, relatively large k_{34} values for $Ru(baph)_3^{2+}$ are, in turn, in accord with the expected view of data for RuL_3^{2+}–D systems.[25] An approximate one order of magnitude increase in k_{34} for the $Ru(baph)_3^{2+}$–R^+ system as compared with $Ru(bipy)_3^{2+}$–R^+ agrees well with that expected from comparison of the $Ru(baph)_3^{2+}$–D and $Ru(bipy)_3^{2+}$–D pair. Differences in k_{34} values between $Ru(bipy)_3^{2+}$–R^+ and $Ru(phen)_3^{2+}$–R^+ pairs are less pronounced similarly to that for $Ru(bipy)_3^{2+}$–D and $Ru(phen)_3^{2+}$–D.

Concluding remarks

The obtained results allow us to conclude that intrinsic differences in the spin conversion rate between the triplet and singlet forms of an activated complex $[RuL_3^{3+/+} \cdots Q^{-/+}]$ are responsible for the quantitative differences in the excited state efficiencies found for the ECL systems involving RuL_3^{2+} complexes. The intuitive relationship between ECL and the electron transfer quenching seems to be quantitatively fulfilled for the ECL processes of the hec type involving $Ru(baph)_3^{2+}$ ion similar to what was previously[12,21] found for $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes. It allows for quantitative predictions of the ECL efficiency in view of the kinetic data resulting from luminescence quenching and transient absorption experiments.

The discussed relationship (although most probable from a kinetic point of view) generally fails in the case of ECL systems of the lec type. The observed difference between ECL efficiencies for the systems of hec and lec types can be only attributed to enhanced rates of the triplet–singlet conversion between $^3[RuL_3^{3+} \cdots A^-]$ and $^1[RuL_3^{3+} \cdots A^-]$ forms. The above conclusion arises from the nearly identical ratios of the ϕ_{es} efficiencies (for the hec and lec types, respectively) found for the ECL systems studied. This finding indicates that ECL systems of the lec type are sensitive to k_{34} values in the same manner as found for hec ones, in contrast to that expected for extremely fast triplet–singlet conversion between $^3[RuL_3^{3+} \cdots A^-]$ and $^1[RuL_3^{3+} \cdots A^-]$.

The observed ECL behaviour (reverse proportionality of ϕ_{es} and k_{34}) strongly suggests that ground state formation is controlled through the k_{34} rate in both types (hec and lec) of ECL systems studied. Consequently, the observed differences between them seem to be attributed to different rates of excited state formation. The ECL efficiencies for systems of the hec type agree quite well with those expected from the k_{23} and k_{32} constants characteristic for the electron transfer quenching. It allows us to conclude that excited state formation in the case of ECL systems of the lec type is kinetically inhibited. The effective rates of excited state formation in ECL systems of the lec type are much slower, as expected from the k_{23} and k_{32} rate constants describing the intrinsic electron transfer step in the quenching reactions leading to a decrease in the observed ECL efficiencies. It supports our previous conclusion that an unknown factor contributes to the overall reaction mechanism. The available experimental data, however, do not permit us to give a more detailed discussion. We hope that the combined studies of solvent and temperature effects will help to solve this problem. Work in this direction is continuing.

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